THESIS

EFFECT OF DESTABLIZED REACTIONS USING LITHIUM AMIDE ($LiNH_2$) AND DOPING USING TITANIUM BASED CATALYST ON THE DESORPTION CHARACTERISTICS OF LITHUIM ALUMINIUM HYDRIDE ($LiAlH_4$)

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ABSTRACT

EFFECT OF DESTABLIZED REACTIONS USING LITHIUM AMIDE ($LiNH_2$) AND DOPING USING TITANIUM BASED CATALYST ON THE DESORPTION CHARACTERISTICS OF LITHUIM ALUMINIUM HYDRIDE ($LiAlH_4$)

In the past few decades there has been a tremendous increase in hydrogen storage research. Numerous materials and material systems have been studied as potential candidates for hydrogen storage, but unfortunately none of those materials demonstrate enough hydrogen releasing capacity under suitable temperature range to be used for hydrogen storage. Research promises to unlock the potential of these materials and ultimately lead to the commercialization of this technology. $LiAlH_4$ is one of those materials that have been exclusively studied as a candidate for hydrogen storage due to its high theoretical hydrogen storage capacity, and its ability to release hydrogen in more than one step at different temperature ranges[1, 2]. Jun Lu and Zhigang Zak Fang[3] studied the effects of titanium based catalyst ($TiCl_3.1/3AlCl_3$) and destabilization reactions using $LiNH_2$ on $LiAlH_4$, but did not demonstrate the effects of ball milling on the system.

In the present work we have investigated the effects of ball milling, and the effects of destabilization reaction using $LiNH_2$ on the hydrogen release characteristics of $LiAlH_4$ doped with $TiCl_3$. The current market scenario for fuel cell technology and the possibility and consequences of introducing the current system in the market has been briefly discussed. X-ray powder diffraction, thermo-gravimetric analysis and scanning electron microscopy were employed for the characterization of the samples. Both the compounds $LiNH_2$, and $TiCl_3$ worked in effecting the dehydrogenation kinetics of $LiAlH_4$. The duration of ball milling

required to affect the dehydrogenation kinetics of $LiAlH_4$ using $TiCl_3$ was optimized. A hydrogen release of 7.3 wt% was observed from the final system i.e. ($LiAlH_4$/ $LiNH_2$ doped with 2% $TiCl_3$) at temperatures below 400^0C.

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Introduction

1.1 Why Hydrogen?

"To truly transform our economy, protect our security, and save our planet from the ravages of climate change, we need to ultimately make clean, renewable energy the profitable kind of energy."

BARACK OBAMA, address to Joint Session of Congress, Feb. 24, 2009

As quoted above our present economy is in an urgent need of a new source of energy that is clean, inexpensive and renewable. Hydrogen can be the next generation of fuels as it has a heating value of (39.3 kWh/kg), which is already higher than most of the common fuels in use today, such as gasoline (13.3 kWh/kg), propane (14.0 kWh/kg) or methane (15.3 kWh/kg). Hydrogen is abundant in our mother planet earth and most importantly it is regenerative and is thus sustainable. Hydrogen undergoes a clean combustion reaction with oxygen ($2H_2 + O_2 \rightarrow 2H_2O$) to produce energy (120 KJ g-1) and water. Since hydrogen is a "carbon free" energy carrier it has a higher energy density than any carbon based fuel. In a combustion reaction (e.g.$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$), the energy contribution from hydrogen is 120 kJ/g^{-1} while the contribution from carbon is only 33 kJ/g^{-1}. Therefore, the energy densities of hydrocarbon fuels scale directly with the hydrogen-to-carbon ratio. To have a direct comparison 3 kg (or 1 gallon= 3.79L) of gasoline carries the same energy as 1 kg of H_2 and moreover, gasoline produces approximately 9 kg of $CO_{2[4]}$ while H_2 produces none. In addition, gasoline is currently made from oil, a finite resource. The increase in demand for oil will likely outpace production within a few decades. Although gasoline can easily be produced from coal through a Fischer–Tropsch process, this method is costly and will likely result in greater greenhouse gas (CO_2) emissions.

Therefore, technologies for clean alternative energy carriers, like hydrogen, need to be developed today to facilitate the transition to a sustainable, carbon-neutral energy economy tomorrow.

1.2 History of Hydrogen

The use of hydrogen as a fuel in engines dates back to the early 19th century. In 1807, a retired French army officer François Isaac de Rivaz designed an internal combustion engine using hydrogen and oxygen mixture as a fuel. A year later, Isaac built one of the first automobiles for his new engine to power. Although the engine was first built by Isaac, it was never commercialized successfully.

This ground breaking invention was followed by a period of hibernation in hydrogen technology until 32 years later the successful working of the first fuel cell was demonstrated by a Welish scientist and barrister Sir William Robert Grove in the February 1839 edition of the *Philosophical Magazine and journal of science* and later sketched, in 1842 in the same journal. The basis of his experiment was the fact that when current is passed through water it splits into its components, hydrogen and oxygen. Robert Grove reversed this process and combining hydrogen and oxygen he could produce water and current. The term Fuel Cell was actually given by two scientists Ludwig Mond and Charles Langer, who attempted to build the first cell using air and industrial coal gas.

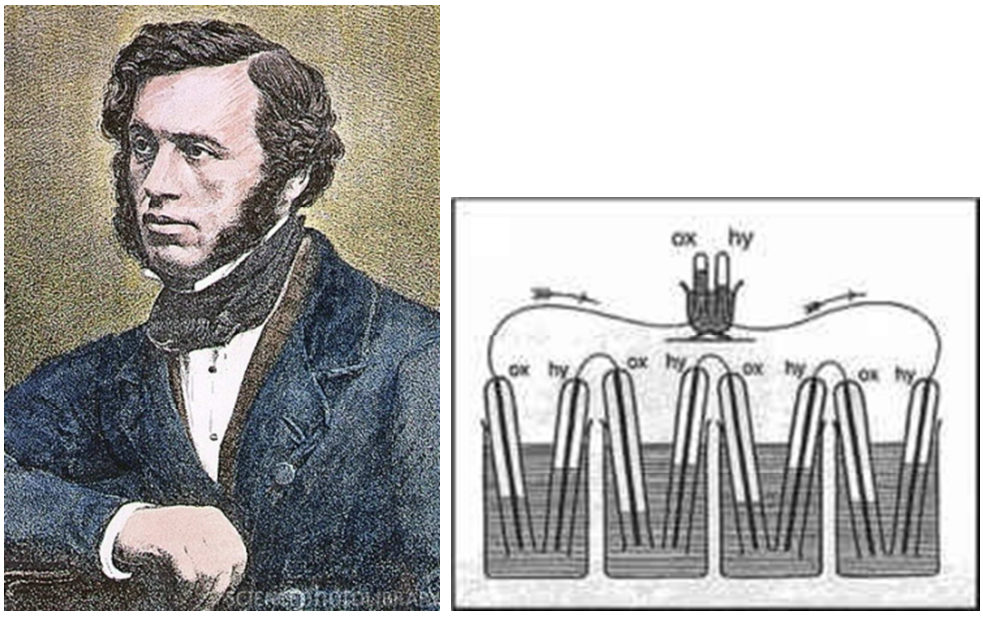

Fig1. A portrait of Sir William Grove and a brief sketch of his design of a fuel cell

This was the dormant period where the use of hydrogen as a fuel in different fields of energy usage was being explored.

In 1898 a scientist named James Dewar experimented with a high pressure hydrogen jet by which low temperatures were realized through the Joule–Thomson effect, and the successful results he obtained led him to build at the Royal Institution, a large regenerative cooling refrigerating machine. Using this machine, liquid hydrogen was collected for the first time, solid hydrogen following in 1899[5].

In the field of space technology liquid hydrogen was first used in the engine designed by Pratt and Whitney for the Lockheed CL-400 Suntan reconnaissance aircraft in the mid-1950s. In the mid-1960s, the Centaur and Saturn space rockets upper stages were both using liquid hydrogen and liquid oxygen as fuels.

As the third quarter of the 20th century progressed there was a gradual realization in the energy industry about the over usage of fossil fuels and the immense need of a suitable substitution for this over exploited and fast diminishing resource.

In the automotive industry General Motors was the company credited to launch the first hydrogen powered vehicle i.e. the 1966 GM Electro van. It was the first ever vehicle to use a fuel cell to power its wheels. The vehicle was a 1966 GMC Handivan on the outside. Its insides were converted into a science lab of new technology that appeared more like a whisky still of old. The GM Electrovan was the brainchild of Dr. Craig Marks who headed up most of General Motors' advanced engineering projects. Marks, along with a staff of 250, developed the Electrovan for over 2 years before attaining a drivable vehicle.

NASA had previously used fuel cells to power onboard systems in their Gemini spacecraft. Those hydrogen fuel cells produced water as a byproduct, which the astronauts were then able to drink.

As a further step to this realization the United States of America founded the DOE (Department of Energy) to set goals and guide lines for research in this new but promising field of renewable energy.

Research in hydrogen technology is reaching its peak in recent years. This is supported by the fact that president Obama wants to double energy efficiency research and deployment, and increase renewable energy research by 70%. Just like his two previous budget proposals, Obama is calling for $36 billion in loan guarantees for traditional nuclear power plants and $2 billion in loan guarantees for renewable energy projects[6].

1.3 Hydrogen Storage Background

The transition of the present economy to a hydrogen based economy will need a lot of technological developments. Hydrogen is an energy carrier (not an energy source) and therefore energy must be generated before hydrogen can be produced. Presently hydrogen is produced from natural gas reforming. This process does not eliminate carbon emissions but simply transfers the source of emissions from the user to the reforming plant. Improvements in the carbon neutral hydrogen production (wind, hydro, solar etc.) fuel cells and the development of a hydrogen production infrastructure is critical in the development of a hydrogen economy. However one of the main technical barriers in the advancement of the hydrogen fuel cell technology for automobile applications is hydrogen storage. The core of the issue is that hydrogen is a gas at standard temperature and pressure (STP) therefore has a low volumetric density. As stated previously, 1 kg of hydrogen is equivalent to 3 kg of gasoline in terms of energy. However, in terms of volume almost 3500 gallons of hydrogen gas is necessary to replace 1 gallon of gasoline. The figures are not much different in terms of liquid hydrogen and there are always Safety issues while storing hydrogen in liquid form at immensely high pressures. Therefore, compressed hydrogen gas and liquid hydrogen cannot meet the aggressive DOE (U.S. Department of Energy) targets.

1.4 Types of hydrogen Storage Technologies

1.4.1 Compressed Gas

Probably one of the easiest ways of storing hydrogen is in its natural gaseous state as a compressed gas in tanks. As in almost all its applications as a fuel, hydrogen is used in its gaseous from, therefore we do not need any additional mechanisms to convert hydrogen to its gaseous form as required in other storage mechanisms such as cryogenic liquid hydrogen storage or metal hydride storage. But this mode of storage has its own disadvantages. As hydrogen is the lightest compound in the periodic table, its weight is considerably less than most of the present day fossil fuels. For example, 3500 gallons of hydrogen gas is required to replace 1 gallon of gasoline in terms of volume. Moreover, storing hydrogen in the form of compressed gas in tanks requires a considerable amount of space, which limits its application to industrial use only. As it requires more space using compressed hydrogen gas for automotive applications is not feasible and it sacrifices the compatibility design of the vehicles. Moreover it creates safety issues storing a highly compressed gas onboard a moving vehicle. The energy density of gaseous hydrogen can be improved by storing hydrogen at higher pressures. This higher pressure requires material and design improvements in order to ensure tank integrity. Advances in compression technologies are also required to improve efficiencies and reduce the cost of producing high-pressure hydrogen. Carbon fiber-reinforced 5,000-psi and 10,000-psi compressed hydrogen gas tanks are under development by Quantum Technologies (figure[2]) and others[7]. Such tanks are already in use in prototype hydrogen-powered vehicles. The inner liner of the tank is a high-molecular-weight polymer that serves as a hydrogen gas permeation barrier. A carbon fiber-epoxy resin composite shell is placed over the liner and constitutes the gas pressure load-bearing component of the tank. Finally, an outer shell is placed on

the tank for impact and damage resistance. The pressure regulator for the 10,000-psi tank is located in the interior of the tank. There is also an in-tank gas temperature sensor to monitor the tank temperature during the

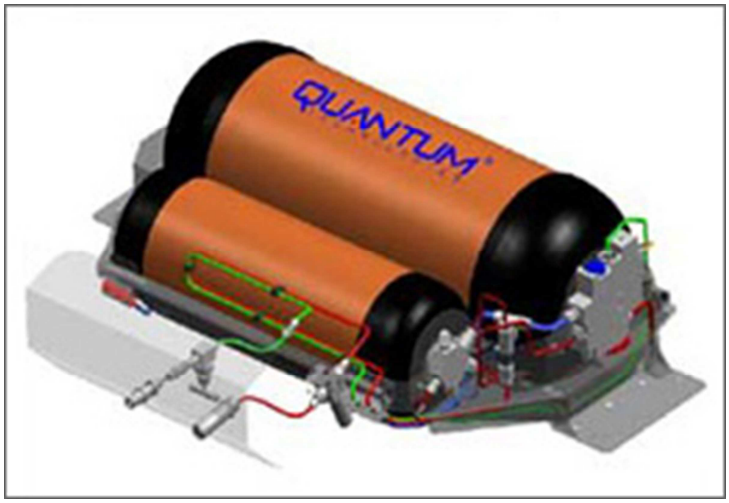

Fig2. A design of a compressed hydrogen gas tank

Gas-filling process when tank heating occurs. Although, big names in the automotive industry successfully developed prototype vehicles in which compressed hydrogen is used as a fuel to run the fuel cell, it's a distant dream of actually commercializing this technology due to design, compatibility, cost, safety and many issues.

The high cost of high pressure compressed hydrogen tanks is mainly attributed to the carbon fiber that is to be essentially used for the low weight structural re-enforcement of the tank. Considerable research efforts are being made to produce such low cost carbon fiber materials that are economical and at the same time which satisfy the tank thickness constraints to meet the volumetric capacity targets.

Therefore reducing the cost and at the same time not compromising on the weight and the volumetric capacity is a key research challenge.

Two methods are being pursued to meet the volumetric and the gravimetric issues of storing hydrogen as a gas. One of them is cryo-compressed tanks. This method is based on the fact that at fixed volume and pressure conditions if the temperature of the tank is reduced the volumetric capacity of the tank increases. It is found out experimentally that if the temperature of the tank is reduced to that of liquid nitrogen the volumetric capacity of the tank can be to four times its original capacity. Although volumetric capacity of the tank in this method is increased, the size of the entire system is also increased because of the cooling system that must be attached to the tank to maintain the tank temperature.

The other approach involves the design of conformable tanks for storing hydrogen gas. Present day vehicles have conformable gasoline or diesel tanks in order to take maximum advantage of the available space in the vehicle. Considerable research efforts are being conducted for the design of conformable compressed hydrogen storage tanks for in board vehicle applications.

In the present day automotive market compressed hydrogen tanks in the pressure range of 5,000 psi (35 MPa) to 10,000 psi (70 MPa) are being certified worldwide according to ISO 11439 (Europe), NGV-2 (U.S.) and many other international safety standards[8].

1.4.2 Cryogenic Liquid Hydrogen

This mode of storage requires hydrogen to be stored at low temperatures in the range of 24K in specialized insulated tanks. Liquid hydrogen has a better advantage

over compressed gas hydrogen in many issues such as energy density, compatibility etc. As it has already being mentioned above that at lower temperatures higher volumetric capacities can be achieved, it can also be mentioned that by storing hydrogen in liquid form, greater energy densities can be achieved at lower operating pressures as compared to compressed hydrogen gas. (figure3)

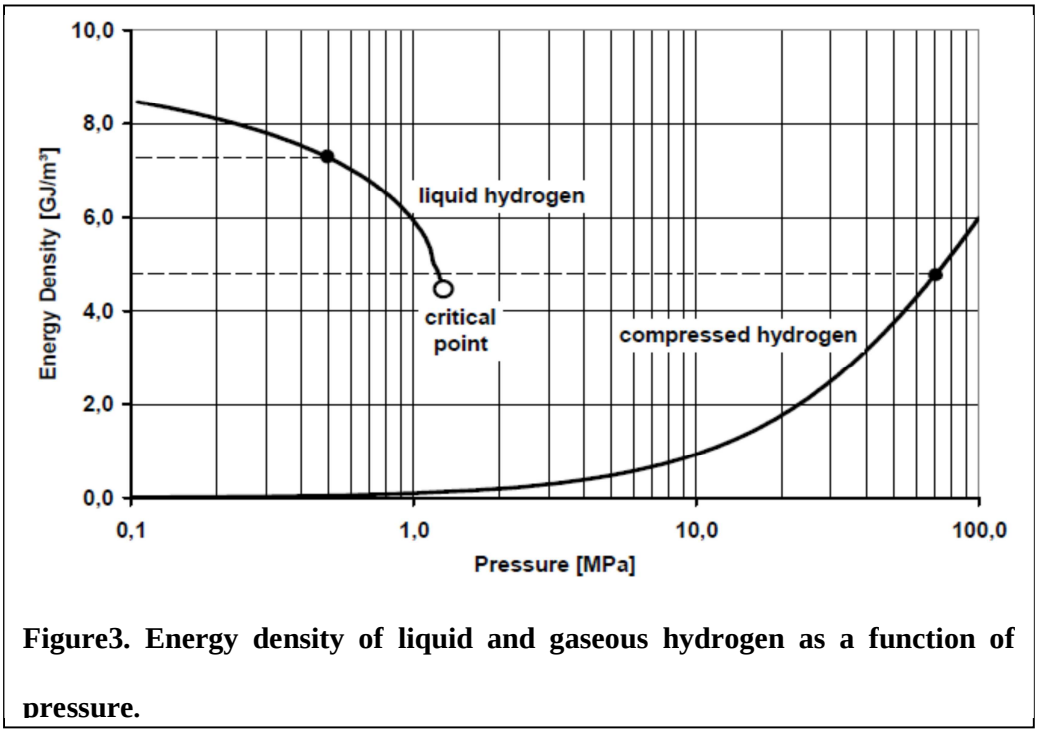

Figure3. Energy density of liquid and gaseous hydrogen as a function of pressure.

It can be clearly seen from Figure 3 that to achieve the energy density of liquid hydrogen at an operating pressure of 0.5Mpa hydrogen gas should be compressed to at least 200Mpa. Having low operational pressures the storage tanks can be better integrated with the vehicle other than conventional cylindrical or spherical designs. In simple terms it is worthy to mention that volumetric capacity of liquid hydrogen is 0.070Kg/L compared to 0.039kg/L at 10,000Psi for compressed hydrogen gas. Though liquid hydrogen is better than compressed hydrogen gas in terms of

gravimetric and volumetric capacities, there are still many challenges in the design of storage tanks for liquid hydrogen such as issues concerning hydrogen boil-off, and the energy required for hydrogen liquefaction. One of the main concerns of using liquid hydrogen as a fuel is the energy to liquefy hydrogen. In general terms this energy is equal to almost 30% of the heating value of hydrogen, this plays a considerable role in the cost of designing the system. Hydrogen boil-off is also an equally important factor as it raises the safety concerns of using the vehicle. So, in order to commercialize this technology, these major obstacles should be reduced or completely eliminated[8].

1.4.3 Metal hydrides

One of the easiest ways of storing hydrogen is in its hydride form. Hydrogen combines with metals, intermetallics and metal alloys to form metal hydrogen compounds. These metal hydrogen combination tales place at ambient temperatures and moderate pressures giving this form of storage critical advantages over the liquid and gaseous forms of storage. The term metal hydride is very vague, as it is the general term given to all the compounds involving hydrogen and metals. There are different classes of compounds within metal hydrides, for example all the transition metals react with hydrogen to give compounds which are basically metallic in nature called transition metal hydrides[5].

Another class of compounds interstitial hydrides are formed when the reaction mechanism involving hydrogen atoms to be present in the interstitial sites of the metal lattice. Nevertheless the differences in their properties, all the metal hydrides are capable of adsorbing and desorbing considerable amounts of hydrogen under the right

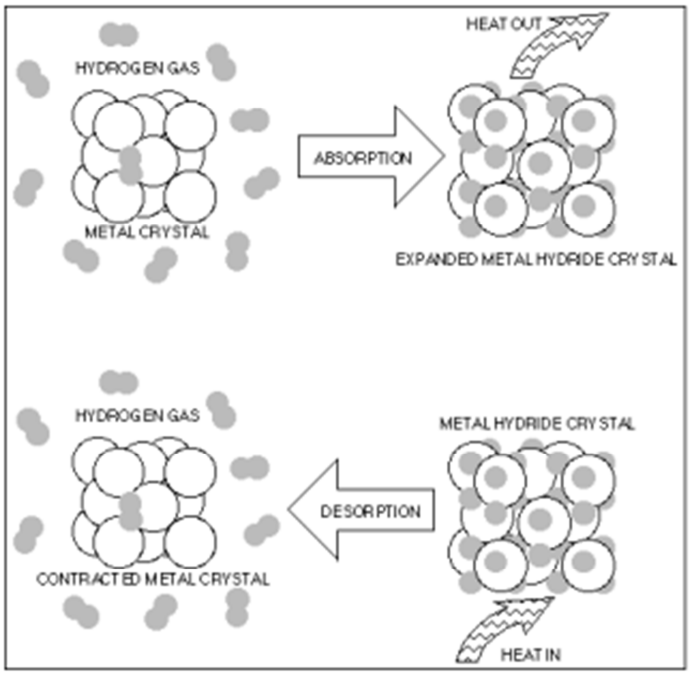

Fig4. Figure illustrating the adsorption and desorption

temperature and pressure conditions without deteriorating. Some metal hydrides can even adsorb and desorb hydrogen close to ambient temperature and pressure. The normal condition of operation of a proton exchange membrane (PEM) fuel cell which uses hydrogen as an operating gas for automotive applications is a pressure of 1-10 atm and 25-120^{o}C. A simple metal hydride such as LiH (Lithium Hydride) has a very good theoretical hydrogen storage capacity of 12.7% of H_2 by weight. It can absorb and desorb 12.7% of hydrogen by weight at temperatures above 700^{o}C and is reversible at high pressures which are way beyond the operating condition of a PEM fuel cell. Other metal alloy hydrides for example $LaNi_5H_6$ have hydrogen adsorption and desorption conditions close to that of the PEM fuel cell but have very low hydrogen storage capacity (~1.4% wt) and are very expensive[5].

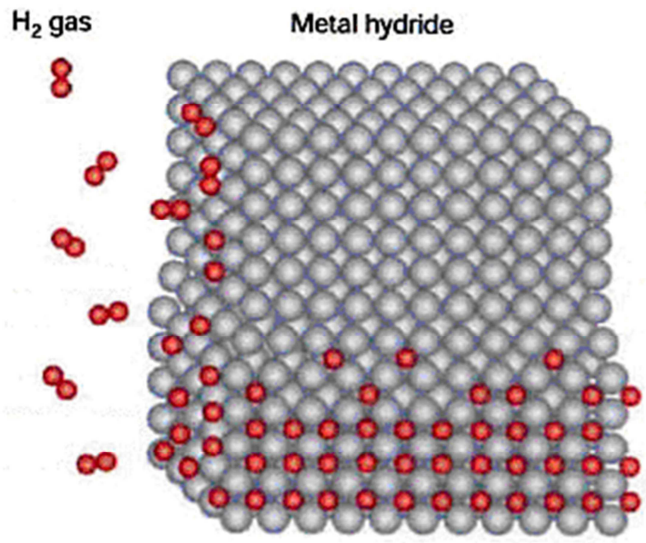

Fig 5: Hydrogen desorption from metal hydride

Probably one of the most studied and researched class of compounds are the complex metal hydrides. These compounds interest the research community because of their high hydrogen storage capacity and the fact that the hydrogen release mechanism in these compounds is through two or more reaction steps. This class of compounds, while having high hydrogen storage capacity can operate in the same conditions as simple hydrides. One of the compounds in this class which sparked the research interest was $NaAlH_4$ (sodium aluminum hydride). Having a theoretical hydrogen storing capacity of around 7.47wt% of H_2 $NaAlH_4$ was initially thought as irreversible in nature and having low reaction kinetics. In the early 1990's it was reported that doping these compounds with Titanium based catalysts could alter the reaction mechanism and reverse the reaction pathway. In 1997 Bodanovic and Swickardi reported that upon catalyzing with $TiCl_3$[2], the reaction kinetics of $NaAlH_4$ were enhanced and could maintain reversibility under moderate conditions in solid state. The reaction pathway can be summarized as follows:

$$3NaAlH_4 \leftrightarrow Na_3AlH_6 + 2Al + 3H_2 \leftrightarrow 3NaH + 3Al + 9/2H_2$$

The problem with this complex hydride was that though its theoretical hydrogen storing capacity was around 7% by weight, the experimental hydrogen release was around 5 % by weight. This was attributed to the fact that some hydrogen stored in the form of NaH was still not released. To desorb hydrogen completely required higher temperatures (around 700^{o}C) and the reversibility of such a reaction required higher operating pressures which are above the operating pressure of a PEM fuel cell.

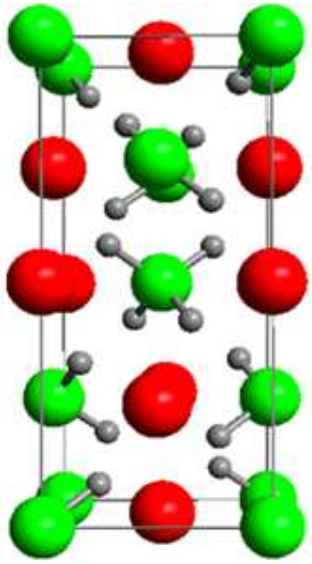

Fig 6. The structure of $NaAlH_4$, the green circles illustrating the Al atoms surrounded by four hydrogen atoms and the red circles indicate the Na atoms in the structure

Recently, a new complex hydride compound $LiAlH_4$ has caught the attention of the research community. Unlike $NaAlH_4$, this compound has a higher theoretical hydrogen storing capacity of around 10wt% of H_2[9] and is more abundantly

available, making it more cost effective than its predecessor. The reaction pathway is similar to that of $NaAlH_4$ and is as follows:

$$3LiAlH_4 \leftrightarrow Li_3AlH_6 + 2Al + 3H_2 \leftrightarrow 3LiH + 3Al + 9/2H_2$$

This reaction pathway faced similar problems to that of $NaAlH_4$, i.e. the completion of the reaction by desorption of hydrogen from LiH under lower operating temperature and pressure, until recently a new set of reactions destabilization reactions reported that reacting LiH with $LiNH_2$ (lithium amide) decreased the structural stability of LiH, allowing it to desorb hydrogen at much lower temperatures[3]. This destabilization reaction is summarized as follows:

$$LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH \leftrightarrow Li_3N + 2H_2$$

This thesis explored the possibilities of these destabilization reactions and the possible effects of doping with a Ti catalyst on the reaction pathway of these hydrogen storage reactions.

1.4.4 Borohydrates

Another class of compounds similar to that of the complex metal hydrides is the metal hydrogen borates commonly referred to as borohydrates. These are the compounds mainly containing the functional group $-BH_4$. Borohydrates have interested researchers because they have the highest hydrogen storing capacity than any class of hydrides in the periodic table. A very good example of this class is $LiBH_4$. Lithium borohydrate has a theoretical hydrogen storing capacity of around 18% wt; it was first synthesized by Schlenger and Brown[5]. The reaction pathway is as follows:

$$LiBH_4 \rightarrow LiH + B + 3/2H_2$$

The desorption of hydrogen from $LiBH_4$ starts at around 320^{o}C and proceeds mainly in the temperature region of 400-600^{o}C with maximum of the hydrogen release around 500^{o}C. Though the theoretical hydrogen storing capacity of $LiBH_4$ is around 18% wt, practically this amount is reduced to around 9% wt which is almost half of the original value[10]. There are two main reasons for this reaction behavior. The first reason is due to the structural difference between $LiBH_4$ and conventional metal hydrides. Unlike the conventional metal hydrides in which the hydrogen atoms are desorbed and adsorbed from the interstitial sites of the metal lattice, $LiBH_4$ exhibits a different structural configuration in which the hydrogen atoms are bonded to the boron atom to form a $–BH_4$ functional group, which when heated releases hydrogen due to the complete decomposition of the parental compound. The second reason is that some of the hydrogen is still stored in the form of LiH which must be further heated to higher temperatures to decompose.

It has recently been reported that catalyzing this reaction using SiO_2 9%wt of hydrogen can be released at temperatures below 400^{o}C[11]. Destabilization reactions of $LiBH_4$ using Mg based hydrides and $LiNH_2$ have also being reported. Nevertheless further research is required to study the reaction mechanisms and reversibility of borohydrates to develop these compounds as a suitable medium for the storage of hydrogen.

1.4.5 Hydrogen storage in Carbon materials

Carbon nano materials are very attractive candidates for hydrogen storage owing to their high specific surface area, microporosity, low mass and high adsorption abilities. Since their discovery in 1991 carbon nano materials have interested the research community in a large way. They are basically graphene sheets with very small inner diameter and a length in the range of 10 to 100 micrometers. Based on their structure they are vaguely classified as single walled carbon nano tubes (SWCNT's) and multi walled carbon nano tubes (MWCNT's).

Single walled carbon nano tubes exhibit a large free volume inside the tube and apart from this, the graphene curvature and the channels between the tubes in a bundle can be potential sites for hydrogen storage.

Apart from the above mentioned new types of nano tubes were discovered from the decomposition of hydrocarbons. These fibrous new materials were called Graphite nano fibers (GNF's).

Hydrogen adsorption form carbon nano tubes were basically experimented at two different temperature ranges i.e. at room temperature and at cryogenic temperature range.

There are a lot of technical papers reporting different types of SWCNT's and MWCNT's having adsorption capacities between the 4 to 6%wt at room temperatures in the pressure range of 10 to 12 MPa, but one of the experiments worth noticing was reported in 1998 by Rodriguez *et al.* This group reported an adsorption capacity of 67%wt using herringbone GNF's. They subjected the sample to hydrogen gas at a pressure of 11.2 MPa in a constant volume and measured over 24 hours[5]. However,

no laboratory was able to reproduce this result. Even at cryogenic temperatures no worthwhile discoveries have being reported.

Probably higher temperatures needed for hydrogen release and the high degree of irreversibility involving chemical hydrogenation of carbon materials are the severe drawbacks from the view point of using them as a potential candidate for hydrogen storage in mobile applications.

1.4.6 Hydrogen Storage in Zeolites and Metal Organic Frameworks

Zeolites are three-dimensional silicate structure in which one or more Si^{4+} ions are isomorphously replaced by Al^{3+} ions with SiO_4 tetrahedrons sharing all four corners of the structure. To maintain the electro-neutrality of this three-dimensional structure there is an additional framework of metal ions adsorbed in the structure. The additional metal ions are usual large cations such as K^+, Na^+, Ca^{+2} or Ba^{+2}. Smaller ions do not occur in the zeolites owing to the large size of the cavities in the lattice structure.

Properties such as honey comb structure with large specific surface area have attracted zeolites to be intensively investigated for a possibility of storing hydrogen in their lattice structure. Several types of Zeolites with different cations have being analyzed for their hydrogen uptake by Langmi *et al.* They reported a highest hydrogen uptake of 1.8 % for NaY at -196^oC and at 15 atm. At room temperature the measured storage capacities were less than 1% wt[12]. The group suggested that the adsorption was due to physisorption.

Although Zeolites have very high surface area and micro porosity in general these materials did not show the expected high adsorption capacities for hydrogen.

Metal organic frameworks or MOF's are extremely porous polymeric structures which consist of metal ions linked together through organic ligands. One of the particularly interesting materials in this class were synthesized by Yaghi and his colleagues and were named nano cubes owing to their cubic structure[13]. They consist of $[OZn_4]^{6+}$ building blocks assembled in a uniform cubic lattice by organic connectors to give rise to a three dimensional structure with were large specific surface area. These blocks are held together by carboxylate groups of linkers resulting in a supertertahedron clusters. The group reported that these compounds have pore densities of almost four times that of the zeolites. Because of their extraordinary properties these structure have being studied for hydrogen storage. Desorption percentages in the range of 1 to 4 % have being reported in extreme range of temperatures and pressures[13]. Further research is required in this field to reduce the adsorption temperatures and pressure to make these materials suitable for hydrogen storage.

1.5 Lithium Aluminum Hydride

Alanates such as $LiAlH_4$, $NaAlH_4$ have being known to man for a long time, but the work of Bogdanovic and Schwickardi who demonstrated the reversibility of $NaAlH_4$ using Ti catalyst brought these compounds into great research interest for their properties as suitable materials for hydrogen storage in automotive applications[2].

Since its first synthesis in 1947 many research groups have studied structural and desorption properties of $LiAlH_4$. In this part of the chapter structural details and the desorption properties are to be discussed in detail.

1.5.1 Desorption Properties

$LiAlH_4$ has a theoretical hydrogen storage capacity of around 10.4%. Unlike conventional hydrides in which desorption of hydrogen from the metal lattice is a one reaction step process, in $LiAlH_4$ hydrogen is desorbed in a 3 step reaction process. The reaction pathway is as follows:

$$3LiAlH_4 \leftrightarrow Li_3AlH_6 + 2Al + 3H_2 \leftrightarrow 3LiH + 3Al + 9/2H_2$$

The maximum amount of hydrogen about 5.3 % is released in the first reaction step of the process and about 2.6 and 2.5% of hydrogen is released in the second and third steps of the process. The last reaction occurs at a temperature above 400^{o}C and was considered not available for practical purposes.

The first and the second reactions occur at temperature ranges of 150-175^{o}C and 180-220^{o}C[2]. It has been reported in several papers that by using very slow heating rates the reaction temperatures can be reduced to 112^{o}C for the first reaction and to about 127^{o}C for the second reaction[14].

Recent technical finding such as destabilization reactions and Ti doping can be used to reduce the hydrogen release temperature in the third reaction. These procedures will be elaborated in the following chapters of this thesis.

1.5.2 Structure

In general the structure of $LiAlH_4$ is described as a distorted tetrahedral structure of AlH_4 ions surrounded by Li ions.

The most stable structure of $LiAlH_4$ before decomposition was reported as monoclinic structure with space group $P2_1/c$ and with hydrogen co-ordination number of four around Al and five around Li ions. Similarly, they also reported the structure of Li_3AlH_6 as Rhombohedral with space group $R\bar{3}$ *[14]*.

1.5.3 Synthesis

LiAlH4 was first synthesized by Finholt and group back in 1947 from the reaction between Lithium hydride (LiH) and aluminum chloride ($AlCl_3$)[15]. The reaction is as follows:

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

In addition to this method, $LiAlH_4$ is prepared industrially from the Meta synthesis of $NaAlH_4$ which is initially prepared from the direct combination of its parent elements by which high yields of $LiAlH_4$ can be produced. The reactions are as follows:

$$Na + Al + 2\,H_2 \rightarrow NaAlH_4$$

$$NaAlH_4 + LiCl \rightarrow LiAlH_4 + NaCl$$

LiCl impurity is removed by filtration from an ethereal solution of $LiAlH_4$, with subsequent precipitation of $LiAlH_4$ to yield a product containing around 1% *w/w* LiCl.

1.5.4 Research Aims:

The aim of this research is to explore the possibilities of new materials for solid state hydrogen storage by studying the desorption characteristics of Lithium Aluminum Hydride (LiAlH4), the effects of doping using Titanium based catalysts on the desorption properties of $LiAlH_4$ and the effects of destabilization reactions using $LiNH_2$ on the desorption properties of $LiAlH_4$.

The specific aims of this project are to:

1. Study the desorption characteristics of the primary material i.e. $LiAlH_4$ and characterize any phases formed in each step of the desorption process as result of desorption of $LiAlH_4$.
2. Determine the changes in the reaction pathway as a result of doping using titanium based catalysts and characterize any phases formed in each step of the desorption process due to the addition of catalyst, and to investigate and optimize the effective ball milling time in the synthesis of the primary material.
3. Determine the changes in the reaction pathway as a result of using $LiNH_2$ to destabilize the reaction and characterize any phases formed in each step of the desorption process due to the addition of $LiNH_2$.
4. Determine the entire % weight of hydrogen release from $LiAlH_4$, with and without the use of catalyst and the destabilization reactions.

Chapter Two:

Characterization and synthesis Techniques

The techniques used in the characterization of metal hydrides, and the working principle of these techniques will be briefly discussed in this chapter. The synthesis methods used in the synthesis of metal hydrides, their working principle and the equipment used in these synthesis methods is also discussed in this chapter.

2.1 Characterization Techniques:

X-ray diffraction:

X-ray diffraction characterization techniques were used as a part of this research mainly to identify the materials formed during the synthesis of the primary materials. This was done by comparing the peaks formed during the x-ray characterization of the materials with the data base.

The diffraction equipment used in this research is a Scintag X-2 advanced diffraction meter equipped with pelteir detector and a stationary sample stage. The materials used in the synthesis are generally sensitive to moisture and atmospheric oxygen, therefore a novel method of x-ray characterization procedure was followed in the characterization of these materials. The procedure makes use of a thin film Mylar sheet, Teflon tape and a single crystal zero diffraction silicon sample holder to prevent the material from reacting with the atmospheric oxygen and moisture. The synthesized material was loaded into the single crystal silicon sample holder inside the glove box. The Mylar thin film and the Teflon tape were then used to seal the

sample holder. Since the sample holder was sealed using the thin film and the Teflon tape the total thickness of the sample holder exceeded the offset height inside the Scintag diffractionmeter. The offset height was readjusted using aluminum braces and thin glass slides. Generally, the x-ray diffraction was carried out from 5^0 to 90^0 using a scanning rate of 4^0 per minute.

Thermo-gravimetric Analysis:

The thermo-gravimetric analysis is one of the main techniques used in the characterization of metal hydride compounds for hydrogen storage. Thermo-gravimetric analysis measures the amount and the rate change in the weight of a material as a function of temperature or time or both in a controlled atmosphere. The measurements are primarily used to predict the thermal stability of the material generally to a temperature of 1000^0C. In this case it is used to predict the weight change in the complex metal hydride as a function of temperature and to predict the desorption temperatures of complex metal hydrides.

Since the complex metal hydrides are very reactive to moisture and atmosphere oxygen a novel method was used in characterization of these materials. The method uses a DSC pan to prevent the material from reacting with the oxygen. In this method a DSC pan and lid with a small hole punctured in the middle of it is preweighed in the TGA equipment and then transferred to the argon glove box. Here, the synthesized material is loaded in to the pan and then sealed properly using a DSC pan sealing equipment. The sealed pan is then transferred to the TGA equipment, which in most of the cases is pre-programmed to heat up to a temperature of 500^0C using a heating rate of 5^0C per minute.

2.2 Synthesis Techniques:

The basic synthesis techniques discussed in this part of the chapter are used in the synthesis of complex hydrides. The two most common synthesis techniques used are chemical synthesis and mechanochemical synthesis, both of which are discussed briefly in this chapter.

1. Chemical Synthesis:

The synthesis of metal hydrides using chemical synthesis is based on factors such as equilibrium between the hydride phase and the precursor phase, operating pressure conditions, operating temperature conditions etc.

It has been reported that Na_3AlH_6 can be synthesized using the chemical synthesis technique in either a one-step reaction process using sodium, aluminum and hydrogen as precursors or in a two-step reaction process using the same precursors varying the reactions pathway for both the methods[16]. The reactions are as follows:

Reaction 1:

$$Na + Al + 2H_2 \rightarrow NaAlH_4$$

$$NaAlH_4 + 2NaH \rightarrow Na_3AlH_6$$

Reaction 2:

$$3Na + Al + 3H_2 \rightarrow Na_3AlH_6$$

In Reaction one which is a two-step reaction process, the first product $NaAlH_4$, is formed form the precursors at a temperature of 270^{o}C to 280^{o}C and at a pressure of approximately 175bar, whereas the final product Na_3AlH_6 is formed at a

temperature of 165^{o}C and at a pressure of 140bar. In reaction two which is a one step process the final product is formed at a temperature of 165^{o}C but a higher pressure of 350bar.

In the chemical synthesis process the final products have to go through a purification process and a vacuum drying process to obtain a pure crystalline product. If the final products formed are sensitive to atmosphere the precursors have to be reacted in another liquid medium and the final products have to be sedimented and later filtered and vacuum dried to avoid contact with atmosphere[16]. This chemical synthesis process is a prolonged process and it takes considerable time and resources to perform these reactions.

2. Mechanochemical Synthesis:

The chemical synthesis method explained above is very tedious and time consuming due to reasons such as long reaction times, and post reaction methods such as vacuum drying, filtration etc. In recent years a new type of synthesis procedure namely mechanochemical synthesis caught the interest of the research community due to its simplicity.

This method, also called solid state synthesis, uses mechanical grinding methods such as manual grinding and ball milling to drive the synthesis reaction[17]. The reaction is mechanically activated due to the high degree of friction and temperature produced due to the grinding process. There are various synthesis procedures in this mechanochemical method depending on factors such as type of ball milling, duration of the milling time etc.

Reactive Ball milling is an effective procedure to synthesize hydrides. In this method the precursors of the hydrides are milled together in a hydrogen atmosphere to obtain the hydrides. The formation of the final hydride differs depending on the milling conditions such as operating pressure and temperature. Doping the reactants with various catalysts can also be realized by using this procedure.

Mechanical alloying is another kind of ball milling procedure in which different hydride powders are milled in order to improve their physical and chemical characteristics such as surface area, reactivity etc. During the mechanical alloying process there is a possibility of change in the physical or the chemical state of the hydrides. This change depends on factors such energy, ball milling time, materials used etc.

Mechanical milling is a ball milling procedure in which there is no change in the physical or chemical state of the materials; it's mainly used to reduce the particle size of the milling materials. Particle sizes in the order of nanometers can be obtained by using this procedure. This method is used for hydride materials because the reactivity of these materials changes with the change in the particle size of these materials.

Ball Milling

A ball mill is a type of grinder, it is a cylindrical device used mainly to grind materials to smaller particle sizes. Ball mills generally rotate around their horizontal axis and are filled with the material to be ball milled and also the material grinding medium. A ball mill generally works on the principle of internal cascading effect, reducing the material to a fine powder.

Fig 7: Laboratory scale ball milling equipment

Fig 8: Industrial scale mall milling equipment

Different materials can be used as a grinding medium such as ceramic balls, pebbles, stainless steel balls etc. Industrial ball mills can work continuously i.e. they are fed on one side and discharged on the other side. Large and medium size ball mills are generally allowed to rotate around their horizontal axis whereas small ball mills consists of a cylindrical capped container attached to two drive shafts. High quality ball mills are very expensive and they can produce particle sizes as small as 5 nanometers.

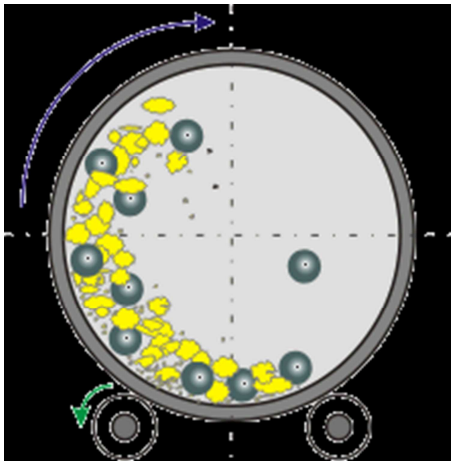

Fig 9: Schematic of ball milling process

The decrease in the particle size of the material has many effects such as increasing the surface area which leads to an increase in the reactivity of the material. The grinding works on the principle of critical speed. The critical speed is generally defined as the speed above which the steel balls start rotating along the direction of the cylindrical container producing no further grinding effect.

Fig 10: Figure illustrating the various kinds of balls used in milling and the different size ball milling canisters

The single most important aspect in the ball milling procedure is the selection of the ball milling medium. The selection of this medium depends on factors that are listed below:

Size: The smaller the size of the ball milling medium, smaller the size of the particles of the material obtained during the milling process. Careful consideration is to be made in selecting the size of the ball milling medium as it should not be less than the largest particle size of the material that is to be milled.

Density: The ball milling medium has to be denser than the materials that are to be milled or else the medium will float on the material during the actual milling process producing no grinding effect.

Hardness: The material of the ball milling medium should be hard enough to produce the grinding effect but not too hard as it might wear out the walls of the ball milling container at a faster pace.

Material: The material of the ball milling medium should be selected depending on the materials that are to be milled so as to avoid any chemical reaction between the material that is to be milled and the milling medium.

Chapter 3:

3.1 Experimental Procedures

This chapter describes the procedure of experimentation conducted as a part of this thesis and also describes the validation of this procedure using a sample material.

The chemicals used for the experiments lithium aluminum hydride, titanium chloride and lithium amide, were purchased from Sigma-Aldrich in hydrogen-storage purification grade and were stored in argon atmosphere glove box to avoid exposure to the atmospheric oxygen.

The experimental procedure included weighing the chemicals using a sensitive balance, mechanical grinding of the chemicals using a pestle and mortar to insure the proper mixing, ball milling the chemicals for predetermined times, characterizing the end product for crystal phases using x-ray diffraction and hydrogen release using TGA. All the above procedures mentioned were carried out under controlled argon atmosphere to avoid contact with oxygen and atmospheric moisture.

3.1.1 Sample Preparation

Complex metal hydrides and their precursors, as mentioned in the previous chapters, have a high affinity for oxygen and atmospheric moisture. Therefore, the entire preparation process is carried out in an argon glove box in which the oxygen and moisture levels are maintained under one parts per million (1 ppm).

To validate the experimental procedure lithium aluminum hydride was selected because ample characterization data is available on it in the literature.

A half gram batch of the starting material was prepared and was mechanically grinded using a pestle and mortar inside the glove box.

3.1.2 Characterization

X-ray Diffraction:

A small amount of the sample was placed in a silicon single crystal - SiZero252520Si zero diffraction plate purchased from MTI Corporation. A Mylar® thin film (gauge: 3.6 μ; 0.00014”; 0.14 mil; 0.00356mm) purchased from Chemplex was used to cover the zero diffraction plate and sealed to using a Teflon tape to properly seal the sample powder in the argon atmosphere and their by avoiding direct contact with oxygen and atmospheric moisture.

X-ray diffraction was conducted using Scintag X 2 diffraction characterization equipment. Alignment of the sample diffraction plate with the sample holding slot in the diffraction equipment was achieved using a metal slide, thin metal braces and thin glass slides specially designed for this purpose. The alignment height was adjusted using the thin glass slides. A quick continuous scan from 5^0 to 90^0 was conducted with a scanning rate of 5^0/ min. Depending on the intensity of the peaks achieved in scan the height was readjusted using the thin glass slides until considerable intensity of the peaks were achieved.

3.2 Validation of Experimental Procedure

3.2.1 Objective

The chemicals being used in the experimental procedure such as lithium aluminum hydride, lithium amide are extremely sensitive to atmospheric oxygen and moisture. Therefore, traditional characterization procedures which expose the sample to air, such as regular x-ray diffraction, thermo-gravimetric analysis cannot be used to characterize these compounds. One has to take special care not to expose these chemicals to atmospheric oxygen and moisture during the characterization process; thus novel TGA and XRD methods, which avoid air exposure, were developed.

The objective of thesis experiments in this section is to validate these novel characterization techniques by comparing the results to available XRD data on these compounds.

3.2.2 Results

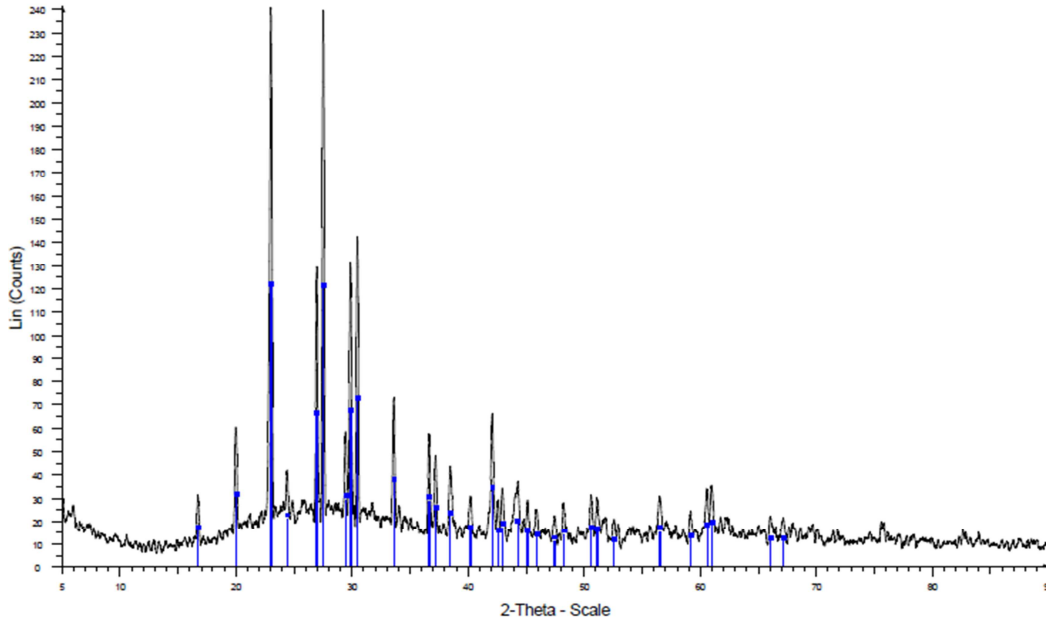

Fig 11: XRD of as-received $LiAlH_4$

Figure 11 is the XRD of as-received $LiAlH_4$. The peaks were compared to the JCPDF database as shown in the figure, which indicate the presence of $LiAlH_4$. Hence, the procedure followed is valid and is repeated for the rest of the systems synthesized as a part of this thesis.

Chapter 4:

Results

4.1. System 1: $LiAlH_4$ ball milled 1 hour

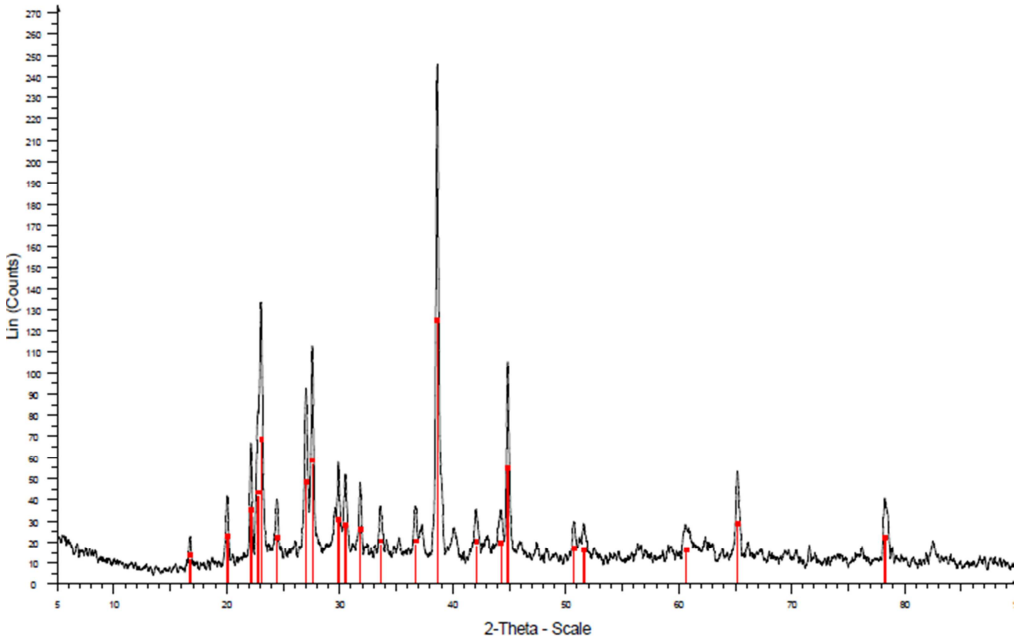

Fig 12: XRD of $LiAlH_4$ ball milled for one hour

Figure 12 is the XRD of $LiAlH_4$ ball milled for one hour. The peaks in the XRD were compared to the JCPDF data base for the presence of $LiAlH_4$.

Thermo-gravimetric analysis was performed in order to provide an overview on the amount of hydrogen desorbed and the critical temperatures at which the hydrogen is getting desorbed.

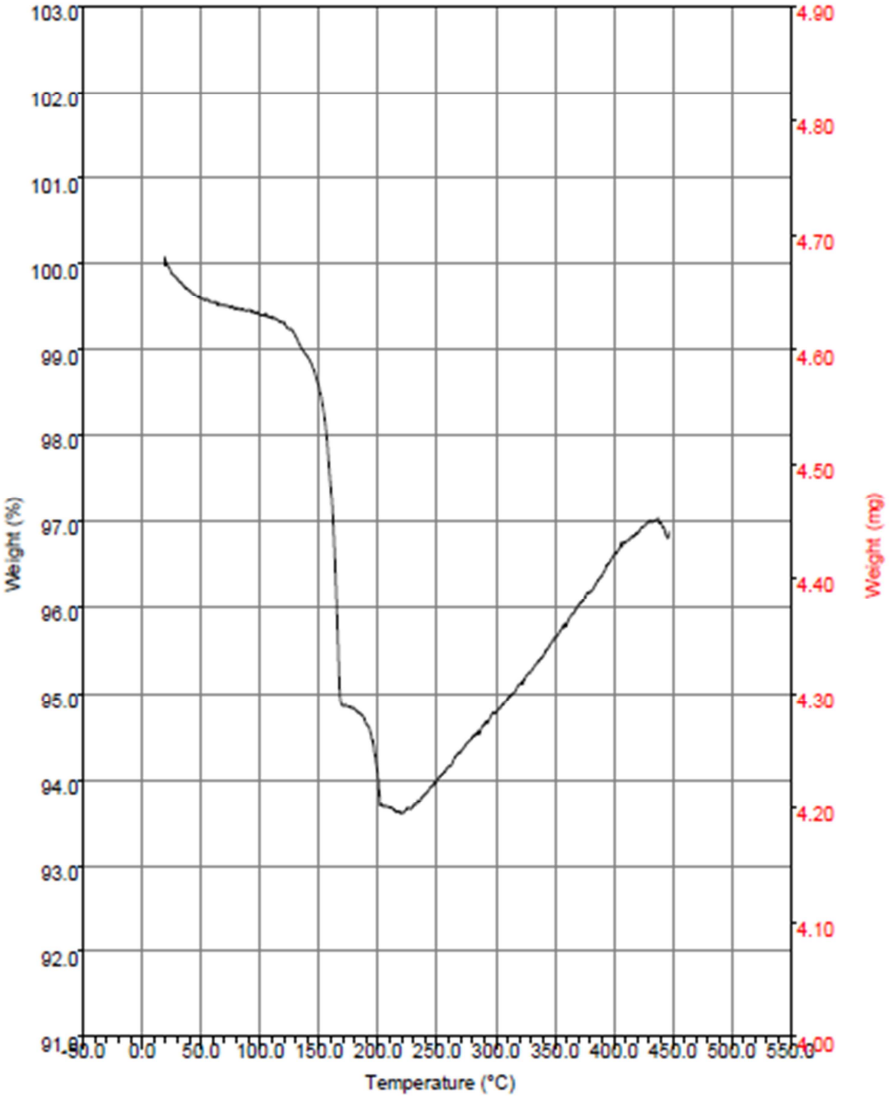

Fig 13: TGA of $LiAlH_4$ ball milled for one hour

Figure 13 is the TGA of $LiAlH_4$ ball milled for one hour. The curve in the figure indicates the percentage of weight lost from the compound due to the heating process from 0^0C to 600^0C using a heating rate of 5^0C per minute.

4.2. System 2: $LiAlH_4/TiCl_3$

The X-ray diffraction analysis is done to resolve the structural composition of the material and to have a XRD pattern of the material.

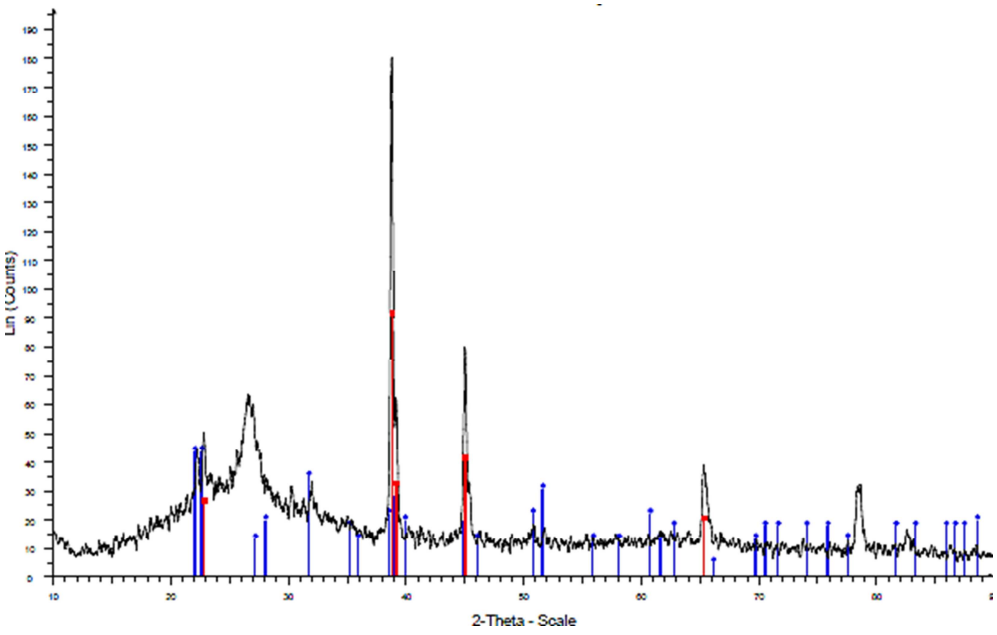

Fig 14: XRD of $LiAlH_4$ doped with 2% $TiCl_3$ and Ball milled for 1 hour

The peaks in the XRD pattern were compared to the JCPDF database and the peaks in the pattern were checked for the presence of $LiAlH_4$, Li_3AlH_6 and trace amounts of $TiCl_3$.

The TGA was performed according to the procedure written in the previous sections under similar heating to a temperature of 400^0C.

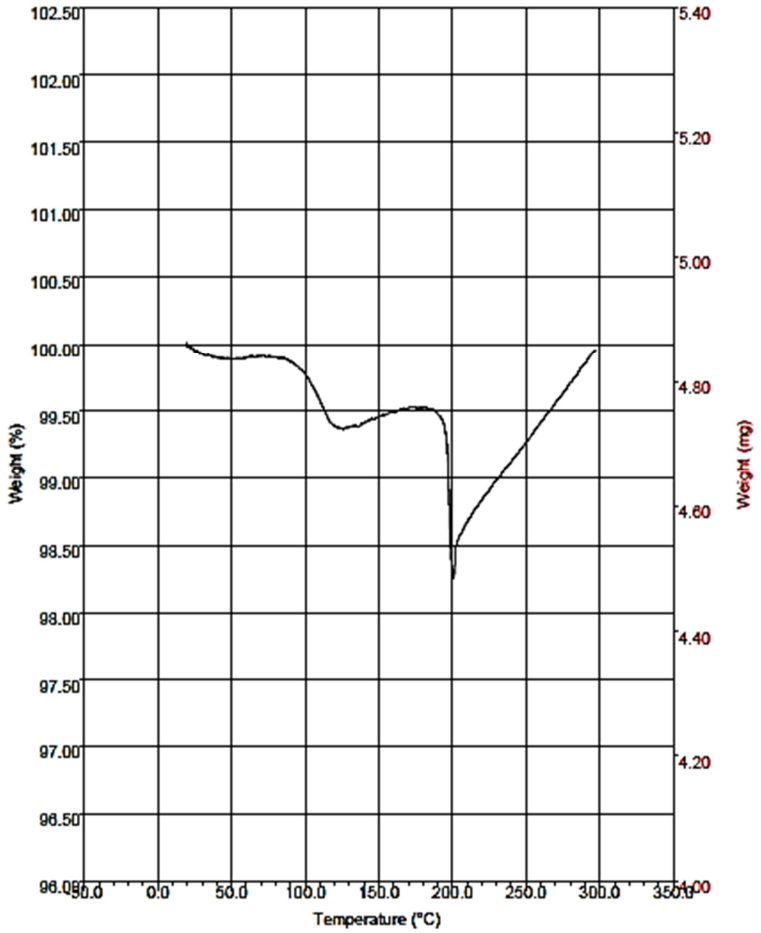

Fig 15: TGA of LiAlH4 doped with 2%TiCl3 and ball milled for 1 hour

Figure 15 is the TGA of $LiAlH_4$ doped with $TiCl_3$ catalyst and ball milled for one hour. The curve in the figure indicates the percentage of weight lost from the compound due to the effect of $TiCl_3$ catalyst when it was ball milled for one hour. The compound was heated from 0^0C to 400^0C using a heating rate of 5^0C per minute.

4.3 Validation of ball milling time

Objective

The objective of this section is to optimize the ball milling time based on particle size. It is cited in literature that the effect of the catalyst on the material largely depends on the particle size of the material and the surface area of the particles in the material[18]. Hence, ball milling procedures are employed to reduce the particle size. One has to note that increased ball milling times can also have a negative impact on the hydrogen release characteristics of a compound[19], as it leads to the excessive pressure built up in the ball milling canister and therefore, leads to the loss of useful hydrogen in the canister. Therefore, it is necessary to optimize the ball milling time for a particular system of material and catalyst.

Experimental procedure

A half gram batch of $LiAlH_4$ doped with 2% $TiCl_3$ was prepared in the glove box and mechanically grinded to insure proper mixing of the material with the dopant. The final product was then transferred to a ball milling canister with 5 steel balls and then ball milled for 30, 60, 90, 120, 150 and 180 minutes using the milling procedure mentioned in the previous sections.

Characterization

Scanning Electron Microscopy

The samples ball milled for various times where collected and part of the samples were loaded to the sample holder of the SEM to measure the particle sizes of the particles in the samples and then gold coated using a thin film vapor deposition technique. The gold coating was performed in order to increase the electrical conductivity of the samples. The size measurements of a minimum of three particles were recorded at a given magnification and the average size of the particle at that particular magnification was measured.

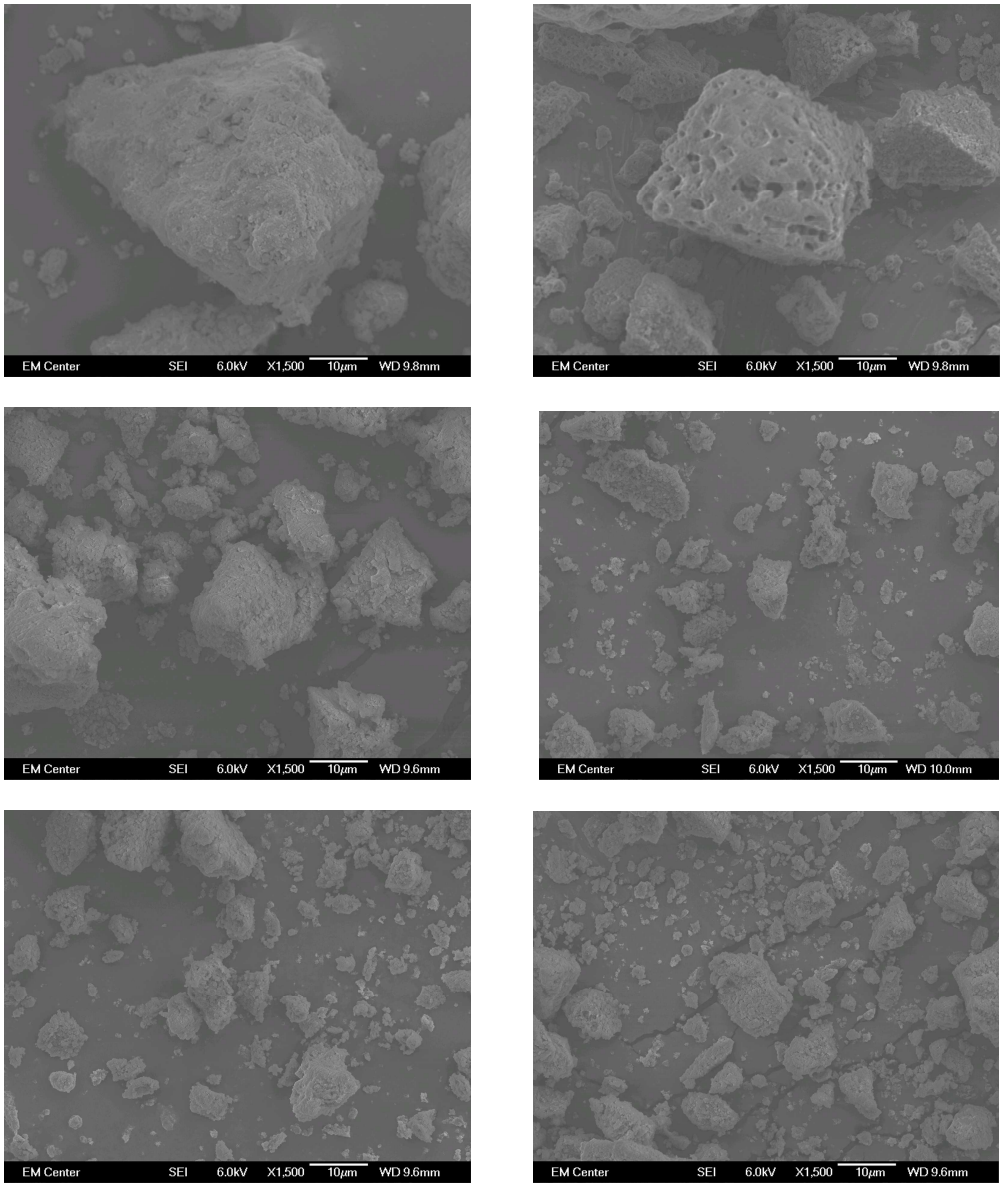

Fig 16: SEM images of $LiAlH_4$ doped with 2% $TiCl_3$ and ball milled for different times at 1500X resolution.

The particle sizes obtained from performing the SEM were plotted against the milling times to obtain a relation between the both parameters. The plot obtained is illustrated in figure 17. Based on the plot the effective ball milling time of 90 minutes was selected.

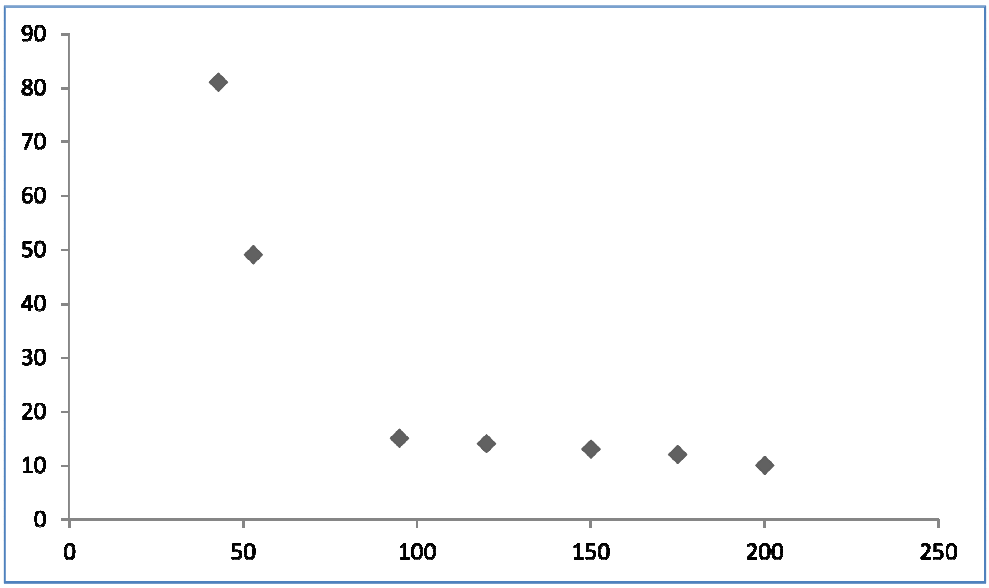

Fig 17: Plot of ball milling time VS particle size

4.4. System 3: $LiAlH_4$ $TiCl_3$

This material was again selected to characterize as the ball milling time was optimized to 90 minutes and the previous time the material was characterized it was ball milled for 60 minutes.

A small amount of the sample was placed in a XRD sample holder and loaded to scintag X2 diffraction equipment and the height of the sample was adjusted using thin metal braces and glass slides using the procedure mentioned in the previous chapter. A scan from 5^0 to 90^0 was performed using a scanning rate of 5^0/min.

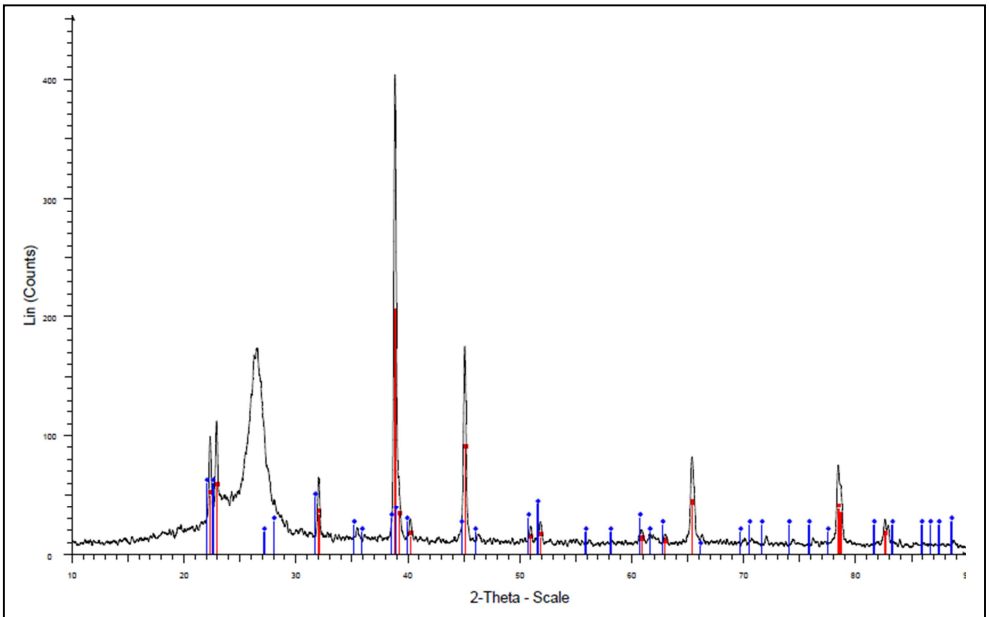

Fig 18: XRD of $LiAlH_4$ doped with $Ticl_3$ and Ball milled for 90 minutes

Figure 18 is the XRD pattern of $LiAlH_4$ doped with 2% $TiCl_3$ and ball milled for 90 minutes. The peaks in the XRD pattern were compared with the JCPDF data base for presence of $LiAlH_4$ and trace amounts of Li_3AlH_6 and $TiCl_3$.

TGA analysis was performed on the sample to measure the amount of hydrogen released and record the decomposition temperature of the various stages in the decomposition process. A small amount of preweighed sample is loaded into a DSC pan which was pre weighed in a TGA equipment. The pan was then sealed in the glove box and loaded to the TGA. The TGA analysis was performed according to the procedure mentioned in the previous chapters.

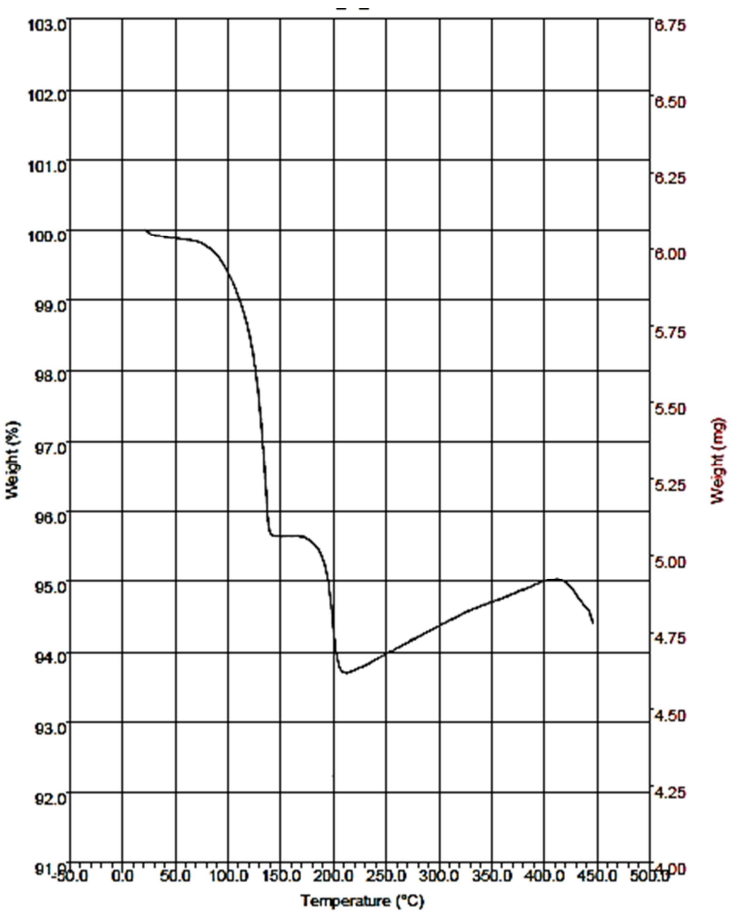

Fig19: TGA of $LiAlH_4$ doped with 2% $TiCl_3$ and ball milled for 90 minutes

The figure 19 illustrates the TGA curve of $LiAlH_4$ doped with $TiCl_3$ and ball milled for 90 minutes. The plot shows the percentage of weight lost by the compound when heated from 0^0C to a temperature of 500^0C.

4.5 System 4: $LiAlH_4$ $LiNH_2$

X-ray diffraction analysis was performed on the material to make a note of the phases present in the material. A small amount of the material was placed in a XRD sample holder and sealed using a Mylar thin film to avoid exposure to the moisture and oxygen during the XRD analysis. The sealed sample holder was then placed in

the Scintag X2 diffraction equipment and the height of the sample was adjusted using metal braces and thin glass slides. A scan from 5^0 to 90^0 was performed using a scanning rate of 5^0/min.

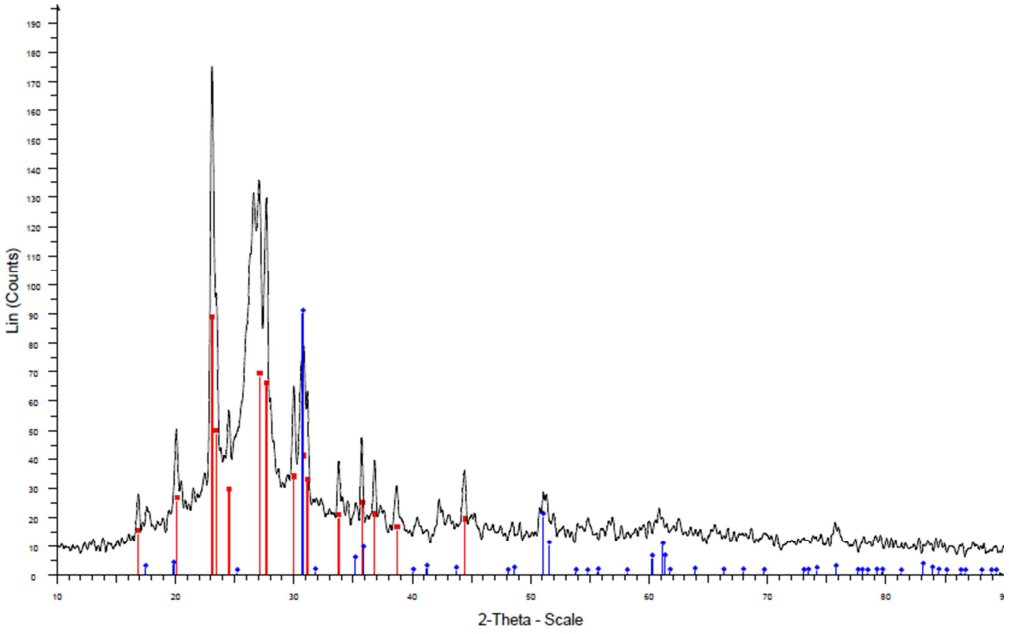

Fig 20: XRD of $LiAlH_4$ $LiNH_2$ as-received

The TGA was performed on the material to record the amount of hydrogen released from the material during the heating process and to estimate desorption temperatures during the heating process.

A small amount of the sample was taken and placed in a preweighed DSC pan with a hole in the center to allow hydrogen gas to escape during the heating process. The loaded DSC pan was then sealed in the argon chamber to avoid contact with moisture and oxygen during the loading of the sample to the TGA equipment.

The sealed DSC pan was loaded in the TGA equipment and programmed to heat to a temperature of 500^0C at a heating rate of 5^0C/min. The results from the TGA analysis are illustrated in the figure below.

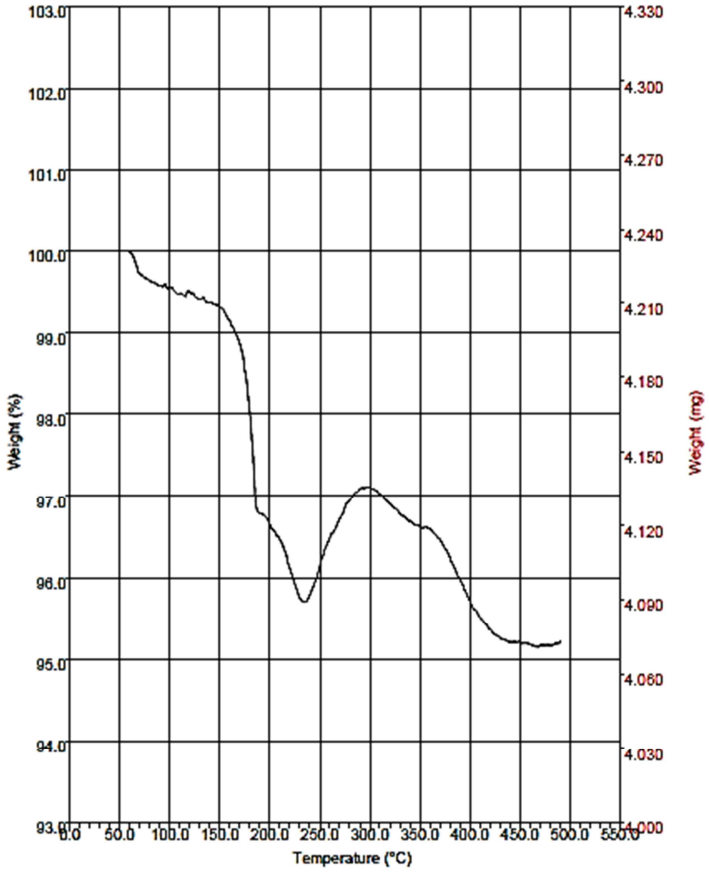

Fig 21: TGA of $LiAlH_4$/$LiNH_2$ As-received

Figure 21 illustrates the TGA curve of $LiAlH_4$ $LiNH_2$ as-received. As the system selected was a mixed system a higher temperature range was selected to allow the reaction to complete.

4.6 System 5: TiCl3 doped $LiAlH_4$ $LiNH_2$

XRD was performed on the sample to make note of the phases in the sample. A small amount of the sample was loaded into the zero diffraction Silicon sample holder and was covered with a Mylar thin film according to the procedure mentioned in the previous chapter. The sample holder was then loaded on to the Scintag X2 diffraction equipment and a scan from 5^0 to 90^0 was performed on the sample.

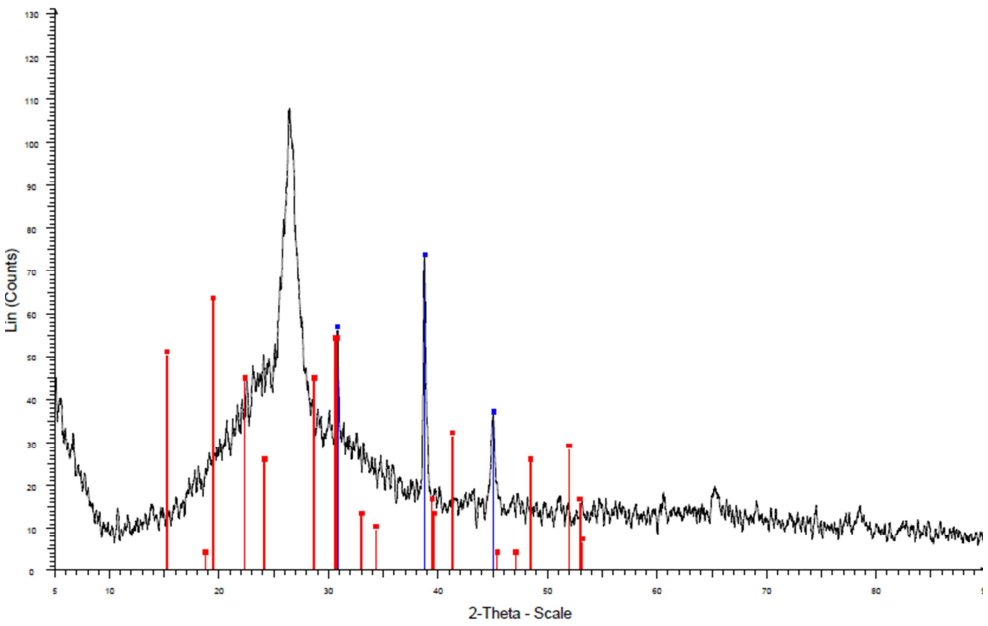

Fig 22: XRD of $LiAlH_4$/ $LiNH_2$ doped with 2% $TiCl_3$ and ball milled for 90 minutes

Figure 22 is the XRD of $LiAlH_4$/ $LiNH_2$ doped with 2% $TiCl_3$ and ball milled for 90 minutes. The XRD was compared to the JCPDF data base to indicate the presence of $LiAlH_4$, $LiNH_2$ and trace amounts of $TiCl_3$ and Li_3AlH_6.

TGA was conducted on the material to estimate the amount of hydrogen desorbed from the material and to record the desorption temperatures of the various stages of decomposition.

The material was sealed in a pre-weighed DSC pan and then loaded into the equipment and was programmed to heat to a temperature of 500^0C using a heating rate of 5^0C per minute.

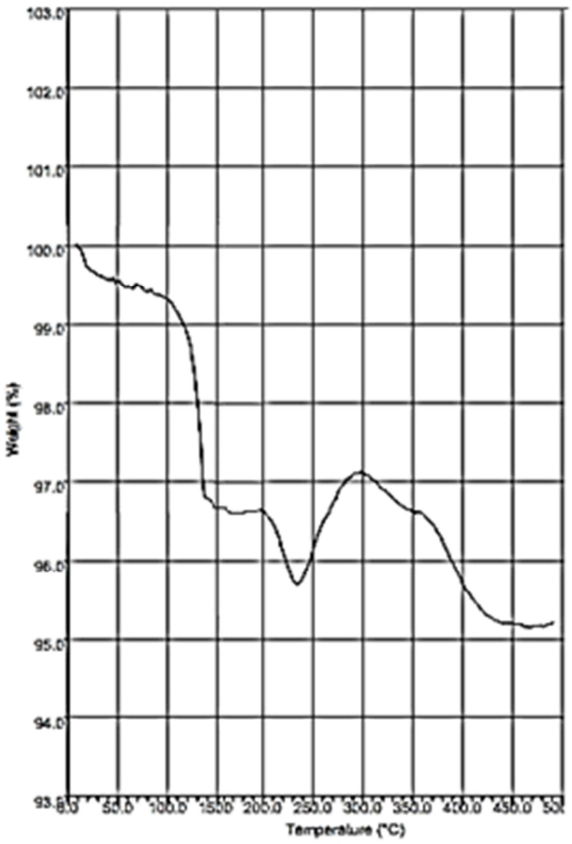

Fig 23: TGA of LiAlH4/ LiNH2 doped with 2% TiCl3 and ball milled for 90 minutes

Figure 23 is the TGA curve of LiAlH4/ LiNH2 doped with 2% TiCl3 and ball milled for 90 minutes. The TGA results indicate the same amount of hydrogen release as from the previous system expect for the shift of the desorption temperature of the second step of desorption i.e. the transition of Li_3AlH_6 to LiH by 50^0C.

4.7 Repetitions

Repetitions have been conducted on the last system i.e. $LiAlH_4$ doped with $TiCl_3/LiNH_2$ to make sure that the primary materials used in the system are of the same composition and to have consistency in the results obtained. Repetitions have been conducted on the assumption that at least two of the results obtained should match with the result obtained from testing the last system i.e. material 5.

4.7.1 Repetition 1: $TiCl_3$ doped $LiAlH_4$/ $LiNH_2$

An initial material of $LiALH_4$ doped with 2% $TiCl_3$ was properly weighed in the glove box and then carefully loaded into a canister having 5 steel balls of varying diameter which is then properly sealed. The canister is then removed from the glove box and then loaded to a ball milled and programmed to milling time of 30 minutes for three times to have a total milling time of 90 minutes. The end products where then transferred to the glove box and then weighed.

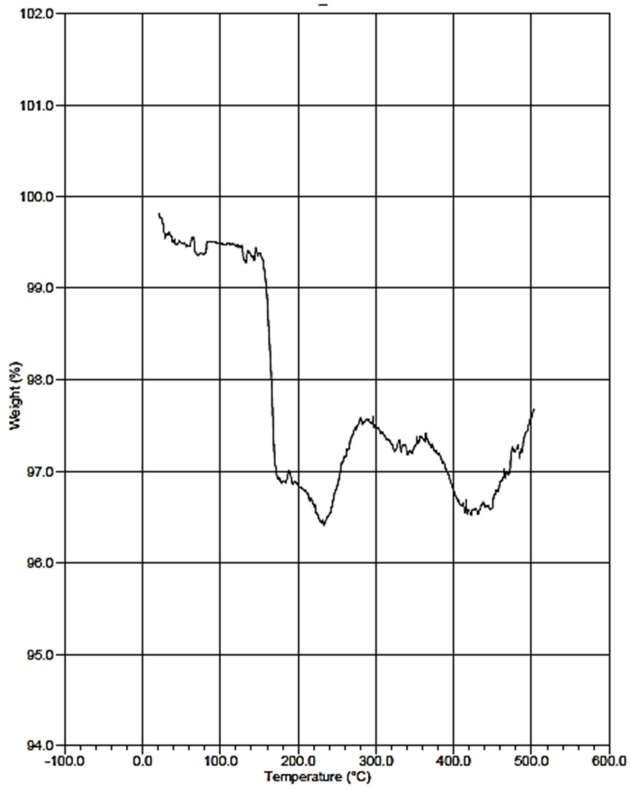

Fig24: TGA of repetition 1

The end material was then mixed with $LiNH_2$ in 2:1 ratio by weight and then hand grinded using a pestle and mortar for 15 minutes to insure the proper mixing of the materials. The final product is then stored for further characterization and testing.

A small amount of the final material is loaded into a preweighed DSC pan with a small hole punched in the center of the lid. The DSC pan was then properly sealed inside the glove box and then transferred to the TGA equipment. The TGA was programmed to heat to a temperature of 500^0C with a heating rate of 5^0C per minute. Figure 24 is the TGA curve of repetition 1. The curve gives the percentage of weight lost from the compound when heated to a temperature of 600^0C using a heating rate of 5^0C per minute.

4.7.2 Repetition 2: $TiCl_3$ doped $LiAlH_4/LiNH_2$

Experimental Methods:

The material was carefully synthesized using the process described in the previous section. Care was taken in measuring the materials, ball milling procedures and hand grinding procedures to insure avoiding any repetition of possible experimental errors that might have taken place during the previous repetition experiment. The final material was then carefully transferred to glass vial and stored for further characterization and testing. The TGA testing was immediately conducted to avoid prolonged storage of the material in the glove box.

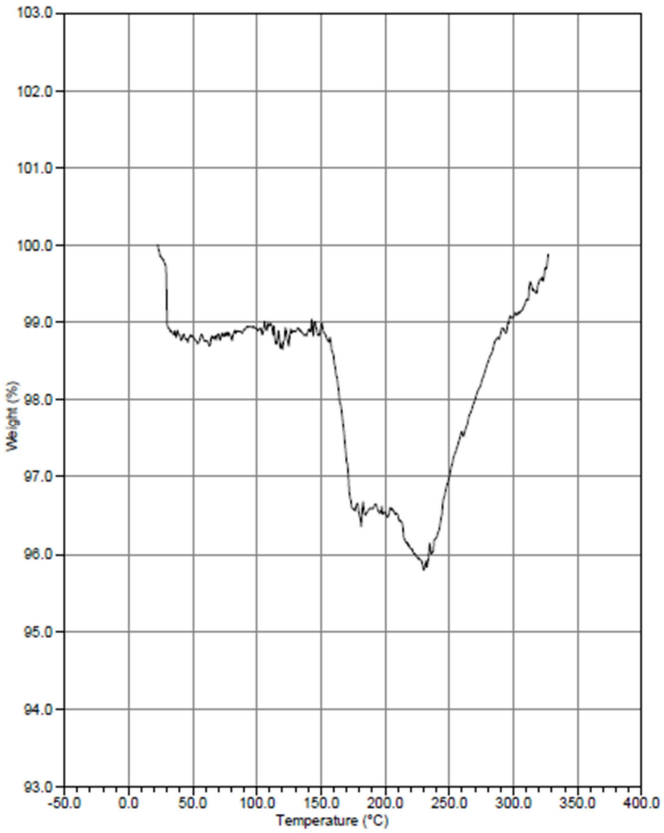

Fig 25: TGA of repetition 2

The TGA was conducted on the material using the same technique described in the previous section heating the material to a temperature of 500^0C with a heating rate of 5^0C per minute.

The TGA from figure 25 resulted in the same amount of hydrogen release as the previous repetition at the same temperature ranges.

The entire results can be summarized using the table below:

Table 1.Summary of results from synthesis

System	Materials	Wt% of hydrogen released	Desorption temperatures
1	$LiAlH_4$ ball milled 1 60 minutes	5.1 %wt	1st step: 70^0C 2nd step: 170^0C
2	$LiAlH_4$ doped 2%TiCl3 ball milled 60 minutes	3.1%wt	1st step: 80^0C 2nd step: 170^0C
3.	$LiAlH_4$ doped 2% $TiCl_3$ ball milled 90 minutes	6.5%wt	1st step: 70^0C 2nd step: 130C
4.	$LiAlH_4$/ $LiNH_2$ hand milled 15 minutes	7.2 %wt	1st step: 70^0C 2nd step: 170^0C 3rd step: 300^0C
5.	$LiAlH_4$/ $LiNH_2$ doped with $TiCl_3$ hand milled for 15 minutes	7.3 %wt	1st step: 50^0C 2nd step: 130^0C 3rd step: 300^0C

CHAPTER 5:

Discussion

In the current study several material compositions of the primary material i.e. $LiAlH_4$ were synthesized and tested based on their hydrogen desorption dynamics. The effect of doping using $TiCl_3$ catalyst on the hydrogen release characteristics of the primary material and on the various compositions of the primary material has been investigated. The effect of ball milling on the material desorption characteristics was studied and the effective ball milling time optimized. Similarly the effect of destabilizing the material using $LiNH_2$ and its effect on the hydrogen release characteristics of the primary material was also studied as a part of the current work.

5.1 *System 1: $LiAlH_4$ ball milled for 1 hour*

This system was considered to be synthesized in order to investigate the first research aim i.e. Study the desorption characteristics of the primary material i.e. $LiAlH_4$, and characterize any phases formed in each step of the desorption process as result of desorption of $LiAlH_4$.To investigate and optimize the effective ball milling time in the synthesis of the primary material. As a starting point in this process a ball milling time of one hour was selected.

The XRD results as indicated in figure 12 suggested the presence of $LiAlH_4$ as expected and also the presence of trace amounts of Li_3AlH_6. The presence of Li_3AlH_6 is due to the temperature built up during the ball milling process. The TGA results as shown in figure 13 suggest a total hydrogen release of 5.7 %wt with two distinct hydrogen releasing temperatures at 70^0C and 170^0C. The primary hydrogen releasing

step is probable due to the decomposition of $LiAlH_4$ to Li_3AlH_6 and the secondary hydrogen releasing step is due to the decomposition of Li_3AlH_6 to LiH. The reactions are as follows:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$$

$$Li_3AlH_6 \rightarrow 3LiH + 3Al + 9/2H_2$$

The results of the TGA and the XRD were in agreement with previously reported literature[20]. The TGA was programmed to run up to a temperature of 600^0C only, which does not allow the complex hydride to completely decompose, because the TGA was conducted using an aluminum pan which melts around 700^0C and running the TGA at temperature exceeding 700^0C would risk damaging the equipment.

5.2 *System 2: $LiAlH_4$ doped using $TiCl_3$*

This material system was synthesized to investigate the second research aim. Previously published work indicates that doping complex metal hydrides such as $NaAlH_4$ and $LiAlH_4$ with Ti based catalyst would enhance the hydrogen releasing capacity of the hydrides at lower temperatures[21]. It was also reported that varying the dopant concentrations would affect the hydrogen release from a material and around 2 to 3% of dopant concentration would optimum in the case of complex metal hydrides[1]. Therefore a 2%$TiCl_3$ doped $LiAlH_4$ material was prepared and ball milled for 1 hour and then tested for hydrogen release.

XRD results as shown in figure 14 indicate the presence of $LiAlH_4$ and trace amounts of Li_3AlH_6 which cannot be avoided due to the ball milling process. The

XRD also reveals the formation of Al_3Ti phase probable formed due to the reaction between the catalyst and aluminum. The reaction is as follows

$$3LiAlH_4 + TiCl_3 \rightarrow Al_3Ti + 3LiCl + 6H_2$$

The TGA results in figure 15 indicate a total hydrogen release of around 3.1 %wt from the material and also indicates the two steps of desorption happening around 70^0C and 170^0C owing to the transformation of $LiAlH_4$ to Li_3AlH_6 and the transformation of Li_3AlH_6 to LiH. The decrease in the hydrogen release is probably due to ball milling time selected in the synthesis of this system. It has been reported that the formation of Al_3Ti is a mechanically activated process, and the ball milling time was probably not enough for the complete phase formation of Al_3Ti[1]. Therefore, there is a need to optimize the ball milling before further investigating the effect of doping on the system.

5.3 *Validation of ball milling time*

The TGA results from the above two sections indicate that ball milling time and the catalyst added have an effect on the hydrogen release characteristics of the material. There was a decrease in the total hydrogen released in the material doped with 2% $TiCl_3$ and ball milled for one hour. Ball milling the material decreases the particle size of the particles present in the material there by increasing the active surface area of the material. Increased surface area aids the catalytic effect on the material[1]. But prolonged ball milling may also lead to the degradation of the material as it results in pressure built up in the ball milling canister and ultimately results in the loss of hydrogen in the canister[19]. Therefore the following study was

conducted to get a relation between the particle size of the material and the ball milling time.

The primary material LiAlH4 was doped with 2% wt $TiCl_3$ and was ball milled for 30, 60, 90, 120, 150 and 180 minutes. The samples were then collected and using SEM the size of the particles present in the samples was recorded as shown in figure16. The particle sizes were then plotted against the ball milling time. According to figure 17 there was no significant change in the particle sizes with ball milling times longer than 90 minutes. Therefore, the optimum ball milling time for the current system was set at 90 minutes.

5.4 *System 3: $LiAlH_4$ Doped with $TiCl_3$*

This system was again synthesized after setting the ball milling time to 90 minutes. There was no noticeable change in the XRD after increasing the ball milling time from 60 minutes to 90 minutes as indicated in figure 23. There was a significant change in the TGA results after increasing the ball milling time. A comparison of figure 13 and Figure 19 shows that there was a total hydrogen release of 6.5 %wt in the material 2 as compared to 5.7%wt for material 1 and a shift of 40^0C was noticed in the first step of desorption of material 2 i.e. in the transition of $LiAlH_4$ to Li_3AlH_6 as compared to material 1. The Difference is probably due to the complete formation of Al3Ti phase which accelerated the formation of Li_3AlH_6 at lower temperatures. Hence, the selection of ball milling time of 90 minutes was validated in this study.

5.5 *System4: $LiAlH_4/LiNH_2$*

This system was selected to synthesize in an effort to destabilize $LiAlH_4$ using $LiNH_2$ and therefore increase the hydrogen releasing capacity of $LiAlH_4$ at lower temperatures as in research aim three. The primary materials were combined in 2:1 ratio and hand milled in the glove box for 15 minutes to insure the proper mixing of the materials, the end product was then tested for hydrogen release.

XRD results of the material indicate the presence of $LiAlH_4$ and $LiNH_2$ phases as indicated in figure 20.

TGA was carried out on the sample to a temperature of 500^0C using a heating rate of 5^0/min results of which indicate a total hydrogen release of 7.2 %wt from the material owing to three distinct steps at 50^0C, 170^0C and at 300^0C as shown in figure 21. The third step is owed to the reaction between $LiNH_2$ and LiH to form Li_2NH which indicates that $LiNH_2$ effectively destabilizes $LiAlH_4$ to form new intermediate compound Li_2NH. The last step of decomposition i.e. the decomposition of Li_2NH to Li_3N was not observed at temperatures below 500^0C, therefore the last hydrogen releasing step is not useful for practical purposes due to its high temperature of release. One can clearly conclude that though the reaction was incomplete, highest hydrogen release was observed in this material compared to the previous material systems.

5.6 *System 5: $LiAlH_4/LiNH_2$ doped with $TiCl_3$*

This material system was synthesized in order to investigate the fourth research aim i.e. the combined effect of doping using the Ti based catalyst and destabilizing using

$LiNH_2$. One can observe from figure 21 and figure 19 that though the as-received system of $LiAlH_4$ and $LiNH_2$ i.e. material 4 had the highest wt% of hydrogen release, the material system 3 i.e. $LiAlH_4$ doped with $TiCl_3$ and ball milled for 90 minutes, had a lower temperature of hydrogen release which is very important for on-board vehicular applications. Therefore, in an effort to combine the advantages of both the catalyst and the destabilizing compound, a combined system having both the $TiCl_3$ catalyst and $LiNH_2$ was prepared and characterized.

The combined system was not directly ball milled as there was a severe pressure built up in the system if $LiAlH_4$ and $LiNH_2$ was ball milled together and eventually there was loss of hydrogen during the ball milling process. To overcome this situation $LiAlH_4$ was first ball milled using 2%wt of $TiCl_3$ and the end product was then mixed with $LiNH_2$ in 2:1 ratio and then hand milled in the glove box to ensure the proper mixing of the materials. The end product was then tested of hydrogen release.

XRD results indicate no significant change from the previous systems i.e. material system 4, except for the presence of trace amounts of Li_3AlH_4 produced during the milling process and also the formation of a Al_3Ti phase as shown in figure 22. In addition to these phases a strong peak at around 27^0C was observed, this was probably due to the partial oxidation of some amount of the material during the XRD characterization..

The effect of combining both the catalyst and the destabilizing material was clearly evident from the TGA results in figure 23 which indicate a total hydrogen release of 7.3 %wt from the material and a shift of 40^0C in the first step of desorption process.

Therefore, in the final combined final system i.e. material 5 there was a total of 2.2%wt increase in the hydrogen desorbed compared to the first material system. The temperature of desorption in the first step of desorption decreased by 40^0C as compared to the first material system.

5.1 Repetitions

Repetitions were done on the material system five which showed the best result, to have consistency in the results that were obtained during the first thermo-gravimetric characterization testing.

Repetition 1: $TiCl_3$ doped $LiAlH_4$/ $LiNH_2$

An initial material of $LiALH_4$ doped with 2% $TiCl_3$ was properly weighed in the glove box and then carefully loaded into a canister having 5 steel balls of varying diameter which is then properly sealed. The canister is then removed from the glove box and then loaded to a ball milled and programmed to milling time of 30 minutes for three times to have a total milling time of 90 minutes. The end products where then transferred to the glove box and then weighed. The end material was then mixed with $LiNH_2$ in 2:1 ratio by weight and then hand grinded using a pestle and mortar for 15 minutes to insure the proper mixing of the materials. The final product is then stored for further characterization and testing.

A small amount of the final material is loaded into a preweighed DSC pan with a small hole punched in the center of the lid. The DSC pan was then properly sealed inside the glove box and then transferred to the TGA equipment. The TGA was programmed to heat to a temperature of 500^0c with a heating rate of 5^0c per minute.

The TGA results indicate a drop in the total amount of hydrogen released from 8.1wt% to 3.7wt% with the 2 steps of desorption taking place 150^0c and 350^0c respectively unlike material system five.

Repetition 2: $TiCl_3$ doped $LiAlH_4/LiNH_2$

The material was carefully synthesized using the process described in the previous section. Care was taken in measuring the materials, ball milling procedures and hand grinding procedures to insure avoiding any repetition of possible experimental errors that might have taken place during the previous repetition experiment. The final material was then carefully transferred to glass vial and stored for further characterization and testing. The TGA testing was immediately conducted to avoid prolonged storage of the material in the glove box.

The TGA was conducted on the material using the same technique described in the previous section heating the material to a temperature of 500^0c with a heating rate of 5^0c per minute. The TGA resulted in the same amount of hydrogen release as the previous repetition at the same temperature range.

This inconsistency in the repetitions is probably due to the prolonged storage of as-received $LiAlH_4$ in the glove box. It is reported that storing unmilled $LiAlH_4$ for a prolonged duration even in inert conditions results in the time prolonged transition of $LiAlH_4$ to Li_3AlH_6[22, 23]. This conclusion is in accordance with the TGA results obtained from both the repetitions where the first step of dehydrogenation i.e. the transition of $LiAlH_4$ to Li_3AlH_6 was completely absent.

One must note that though last material system i.e. material 5 showed good improvement in the hydrogen release characteristics, these experimental results can further be improved by improving the experimental conditions and procedure i.e. conducting the entire characterization experiments (XRD, TGA) in inert atmospheric conditions. Further study based on varying the $TiCl_3$ concentrations on the primary material i.e. $LiAlH_4$ and exploring the possibilities of combining other transition metal catalysts with $LiAlH_4$ is highly recommended. Another area which needs to be explored is the reversibility of the final material system i.e. recombining the final products to get the primary materials at normal pressures. This area of reversibility needs to be explored and studied before making this material system suitable for practical purposes.

Chapter 6:

Current system for automotive applications

One of the motivations for the current research work is the application of complex metal hydrides as a hydrogen storage medium in automotive application. The automotive industry is changing rapidly due to the current scenario of depleting fossil fuel resources. The debate of replacing the fossil fuel runs vehicles with a more renewable and sustainable source of fuel has being running for almost several decades. Alternate sources of fuel such as bio gas, solar energy and hybrid electric vehicles run on both gasoline and electricity from battery packs. NiCad and Lithium ion battery technology have been considered but they proved to be more of a temporary replacement of fossil fuels rather than a permanent one because of problems such as long recharging times and short miles range etc.[24]. One of the technologies which proved to be a top contender for replacing the fossil fuels is the fuel cell technology. This fuel cell technology has the advantage over the electric vehicles as it has low recharge times and longer range compared to the electric vehicles[25].

The main challenge of commercializing this technology is the onboard storage of hydrogen in the vehicle[5]. Research in this field for the past few decades have come up with 2 main ways of storing hydrogen in these fuel cell vehicles i.e. through compressed gases and in the form of hydrides (metal hydrides, complex metal hydrides, MOF's etc.). The research conducted as a part of this study was an effort to apply the complex metal hydride in the present study ($LiAlH_4$) as a hydrogen storage medium in fuel cell vehicles.

6.1 Current Market Scenario:

In the current automotive market big companies such as General Motors, Toyota etc. have come up with their version of the fuel cell vehicles. Honda's version of the fuel cell vehicle i.e. the Honda FCX is soon to be launched commercially. According to the company specifications, the Honda FCX stores hydrogen onboard as compressed gas stored at a pressure of 5000psi which has an effective hydrogen volumetric storage efficiency of ~23g H_2/L and can store up to 3.92 kg of hydrogen per tank. The Honda FCX also claims to have a vehicle range of 240 miles. Toyota's FCHV fuel cell hybrid vehicle which is due mass production in the United States this year stores compressed hydrogen gas a pressure of 70Mpa i.e. 10000psi which improves the volumetric storage efficiency to around 39g H_2/L and also has a possibility of higher vehicle range of around 300 to 400 miles per tank. General motors took one step further by letting the consumers to test drive its version of the fuel cell car i.e. the Chevrolet Equinox which according to the company's specifications has an option of using either the 5000psi tank or the 10000psi tank and stores up to 4.2 kg of hydrogen per tank.

6.2 $LiAlH_4$ as a medium for hydrogen storage

One of the main challenges of implementing $LiAlH_4$ as an onboard hydrogen storage medium is its reversibility. In the current research work the reversibility of $LiAlH_4$ has not been studied but it has being reported in previous research work that $LiAlH_4$ doped with Ti based catalyst has a reversibility of above 6.5%[26]. Taking into consideration the possibility that $LiAlH_4$ reversibly stores at least 6% of hydrogen by weight we can calculate and study the possibility of using $LiAlH_4$ doped $TiCl_3$ as a

medium for on board hydrogen storage. To replace the compressed hydrogen gas with metal hydride storage, the parameters such as volumetric storage capacity, amount of hydrogen stored per tank and ultimately the miles range that can be obtained per tank have to be studied.

Taking into consideration the current system i.e. $LiAlH_4$ doped with 2% $TiCl_3$ and ball milled for 90 minutes we assume that it can at least store 6% weight of hydrogen reversibly, the following calculations have being performed on the system. Considering the density of $LiAlH_4$ i.e. 0.917gm/cm^3 and assumption that 6%wt of hydrogen can be reversible stored in it the volumetric efficiency of the system is calculated as 0.055 kg/L i.e. 0.55kg of hydrogen can stored per liter of the material. Taking into consideration the tank specification of the fuel cell vehicles available in the market and applying for the current material a total of 7.04 kg of hydrogen can be stored onboard at any time. This implies that using the current system as medium for onboard hydrogen storage, a miles range of 400 miles per tank can be achieved. Listed below is the list of parameters calculated compared to storing hydrogen as a compressed gas at 5,000psi and at 10,000psi.

Table 2. Table illustrating the parameter values compared to compressed hydrogen

	$LiAlH_4$ $TiCl_3$ ball milled 90 minutes	Compressed Hydrogen at 5,000psi	Compressed Hydrogenat 10,000psi
Volumetric efficiency	55g H_2/L	23g H_2/L	39g H_2/L
Weight of H_2 stored per tank	7.02 kg	3.92 kg	4.2 kg
Miles range	~400	240	300-400

Though the current system is promising as a candidate for onboard hydrogen storage it has a few materialistic and design issues which need to be studied before implementing this technology industrially. One of the main problems is that though $LiAlH_4$ has theoretical hydrogen storage capacity of around 10.6wt% the total amount of hydrogen cannot be used for practical purposes. The reason behind this is that $LiAlH_4$ desorbs hydrogen in three distinct steps and last step i.e. the desorption of LiH takes place at temperatures well above 400^0C which cannot be used for practical applications thereby reducing the usable hydrogen to around 6.5wt%.

Another challenge is the reversibility of $LiAlH_4$. Complex metal hydrides such as $NaAlH_4$ have sparked interest in the research community back in the 90's as they showed reversibility in the presence of Ti based catalyst. Since then, a lot of research effort has been put in demonstrating the reversibility of $LiAlH_4$, as it has a higher hydrogen storing capacity than $NaAlH_4$. Initially $LiAlH_4$ was termed as irreversible as the first step in its desorption process i.e. the transformation of $LiAlH_4$ to Li_3AlH_6 is an exothermic process unlike other complex metal hydrides. Therefore this reaction could not be reversed until recently it was reported that $LiAlH_4$ can be indeed reversed in the presence of $TiCl_3$ and an organic compound $MeO_{2[26]}$. Still a lot of work needs to be done to establish the credibility of reversing $LiALH_4$.

The last and the foremost challenge is the design of the storage tank for onboard storage of hydrogen. The tank should be designed in such a way that it can retain the heat from the fuel cell to desorb the hydrogen as well as to release any excess heat produced in the tank to a heat sump. The following is a schematic of a system utilizing the storage tank described above.

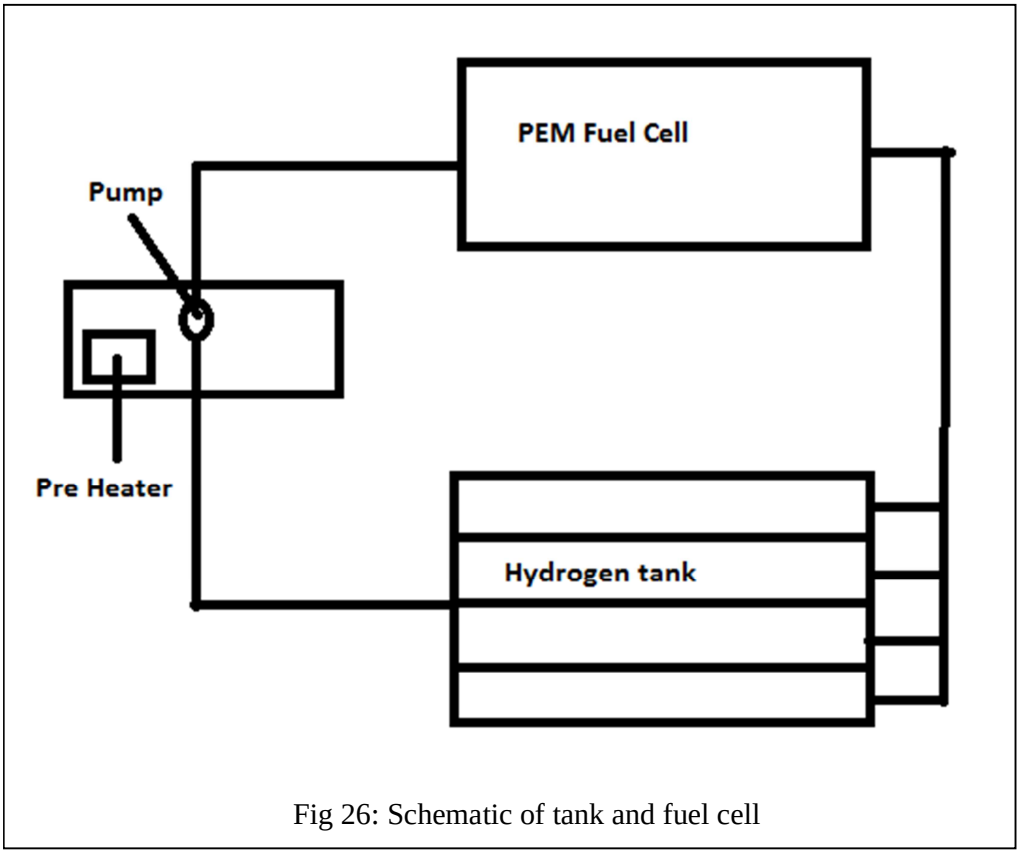

Fig 26: Schematic of tank and fuel cell

The system uses a heat transfer fluid and a pump mechanism to transfer the heat from the fuel cell to the hydrogen storage tank. The schematic also has a preheater mechanism to help provide the necessary heat to the tank during the starting of the vehicle. Since the hydrogen from the current system is released in the temperature range of 50^0C to 200^0C, a high temperature operating PEM fuel cell with an operating temperature of around 125^0C to 250^0C is most likely to be used in the current model.

Chapter 7:

Conclusion and future work

7.1 Conclusion:

The current research work was an effort to explore new materials for hydrogen storage, mainly for on board vehicular application. Many material systems of the primary material i.e. $LiAlH_4$ have been synthesized and tested for hydrogen release characteristics. Novel methods of XRD and TGA characterization were developed in the current study to suit the current materials under consideration, which are sensitive to atmospheric moisture and oxygen.

The dehydrogenation properties of the primary hydride i.e. $LiAlH_4$ were studied as a part of the research aim one.

To study the effect of catalyst on the hydrogen desorption properties of $LiAlH_4$ according to research aim two, a transition metal catalyst $TiCl_3$ was selected. The effect of ball milling on $LiAlH_4$ was also tested and an effort was made to optimize the ball milling time for the current system i.e. $LiAlH_4$ doped with $TiCl_3$.

A sample containing the material was ball milled for different times and SEM was conducted to record the particle sizes of the different ball milled samples. By plotting the ball milling time VS the particle sizes, an optimum ball milling time of 90 minutes was selected. The effects of destabilizing reactions using $LiNH_2$ on $LiAlH_4$ were also explored as a part of research aim three. A desorption temperature shift of 40^0C was observed in samples containing 2% $TiCl_3$ and ball milled for 90 minutes.

Highest hydrogen release of 7.3 wt% of hydrogen was observed in material 5 i.e. $LiAlH_4$/ $LiNH_2$ doped with $TiCl_3$ and ball milled for 90 minutes as a part of research aim five.

A brief study of the current fuel cell market scenario was conducted and the practical implications of introducing the current technology in the market were also explored. A preliminary design which combines the metal hydride storage system with a high temperature fuel cell was also proposed.

7.2 Future Work:

On the basis of the results obtained throughout the course of this research, the following recommendations for future work can be made:

- Further investigation into the effects of other transition metal catalysts on the dehydrogenation characteristics of the current system.
- Investigation into other destabilization reaction systems dealing with $LiAlH_4$ such Mg-$LiAlH_4$-$LiNH_2$ etc.
- Investigation into the re-hydrogenation of $LiAlH_4$ using the catalysts mentioned in the previous section and determining a standard procedure of re-hydrogenating such systems in the lab under controlled pressure conditions.
- Investigation into developing new ball milling procedures to avoid pressure builds up during ball milling, or development of other techniques for decreasing particle size and increasing surface area of the precursors.
- Determination of heat analysis on the storage tank during hydrogen release and uptake.

- Determination of the overall efficiency of the fuel cell storage tank system and optimization of the design.

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